Electrochemical Pretreatment for Microfiltration of

Surface Water: Mechanisms of Fouling and Its Control

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In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in Environmental Engineering

by

Neranga Pitiduwa Gamage

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Surface Water: Mechanisms of Fouling and Its Control

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Abstract

Aluminum electrochemical pretreatment was evaluated for fouling control during surface water microfiltration (MF) using bench-scale galvanostatic batch electrolysis experiments followed by constant pressure, dead-end MF. In all cases, electrochemical aluminum production quantitatively obeyed Faraday's law with a 3-electron transfer at nearly 100% efficiency. Underlying physical and chemical mechanisms were delineated using a variety of characterization methods including Attenuated total reflectance – Fourier-transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), electron microscopy, light scattering, and colorimetry.

Fouling of a commercial polymeric MF membrane following electrocoagulation was found to (1) be lower at pH 6.4 compared with 7.5, (2) decrease only up to an intermediate aluminum dosage, and (3) exacerbate with increasing transmembrane pressure. In all experiments, cake filtration was the predominant flux decline mechanism for the entire duration of MF. Fouling was controlled by antagonistic effects of adding more and more aluminum coagulant; increasing total mass loading of colloidal foulants (higher *total* filtration resistance) and creating larger and more porous flocs (decreasing *specific* cake resistance). Cathodic production of hydrogen bubbles induced floc flotation over relatively long durations of electrolysis. Such electrochemically assisted flotation - "electroflotation," was employed for MF pretreatment and this approach increased permeate fluxes better than electrocoagulation (i.e., flotation was not utilized) by reducing both the cake mass and the cumulative hydraulic resistance.

Physically irreversible fouling and fouling control after electroflotation pretreatment was investigated using ATR-FTIR and XPS. Hydrophobic molecules primarily appeared to initiate physically irreversible fouling during untreated raw water MF. Electroflotation pretreatment

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reduced fouling by decreasing foulants pore penetration and accumulation of hydrophobic, proteinaceous, carbohydrate-like, acidic, and siliceous molecules.

Differences in physical and chemical characteristics between various MF feed water colloids including untreated raw water and flocs generated during electrochemical and chemical coagulation were used to rigorously deduce their contributions to observed differences in cake compressibility. (Electro)coagulation generated cakes that compacted significantly at higher pressures compared with raw water. Cake compression in pretreated waters included elastic contributions from gelatinous and fluffy, amorphous Al(OH)_{3(S)} solids (as determined by XRD and microscopy). Electrocoagulated flocs were more porous (due to hydrogen bubbles attachment) and fragile (from greater presence of hydrophobic compounds and lower amounts of amides and acidic organics) compared with those generated by alum coagulation. Hence, they are expected to be more prone to break and rearrange at high pressures and contribute inelastically to cake collapse and compressibility.

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Nomenclature

ТМР	Transmembrane Pressure
MF	Microfiltration
UF	Ultrafiltration
NOM	Natural Organic Matter
DBP	Disinfect Byproducts
DOC	Dissolved Organic Carbon
UV	Ultraviolet
RLA	Reaction Limited Aggregation
DLA	Diffusion Limited Aggregation
RGD	Rayleigh–Gans–Debye Theory
BE	Binding Energy
TDS	Total Dissolved Solids
EC	Electrocoagulation
EF	Electroflotation
R _a	Aggregate Radius and the Primary Particle
R _p	Primary Particle Radius
d _{f,2D}	2D Fractal Dimension
d _{f,3D}	Mass Fractal Dimension
Ν	Minimum Number of Square Boxes Required to Completely Cover the Aggregate
L	Box Size
q	Scattering Vector
n	Refractive Index of the Suspension
λ	Wavelength

J	Flux
J ₀	Clean Water Flux
t	Time
V	Cumulative Volume Filtered
A _m	Membrane Area
α*	Specific Cake Resistance on a Mass Basis
α* ₀	Specific Cake Resistance at an Unstressed State
n	Compressibility Index
ΔΡ	Transmembrane Pressure
μ	Absolute viscosity of Water
C _b	Bulk Solids Concentration
R _m	Clean Membrane Resistance
m	Mass in Grams of Al Generated
I	Current
F	Faraday's Constant (96 486 C eq ⁻¹)
Z	Number of Electrons Transferred per Al Atom

Chapter One. Background and Research Objectives

1.1. Introduction

Rapid growth in population and industrial activities, increasing identification of new contaminants, land subsidence triggered by excessive ground water extraction, and diminishing availability of clean water sources demand advanced technologies such as membrane filtration for water and waste water treatment. Stricter regulations, the major *Cryptosporidium* outbreak in 1993 and technological improvements resulted in rapid growth of low pressure (typically less than 1 – 2bar) membranes such as microfiltration (MF) and ultrafiltration (UF) for drinking water treatment (Furukawa 2008, Huang et al. 2009). However, fouling, the resistance buildup against water passage through the filter due to deposition of materials, limits the performance of membranes. Fouling can be controlled by either, (1) changing the feed water characteristics such as surface charge, particle size distribution, fractal dimension, and chemical composition (2) changing the membrane properties like surface chemistry, morphology, and geometry of the membrane matrix, and/or (3) physically and chemically regenerating the membranes through periodic backwashing and chemical cleaning. While low pressure membranes are highly effective in removing turbidity, bacteria and protozoa, they are not as effective in removing viruses and disinfection byproduct (DBP) precursors.

Coagulation of feed waters using hydrolyzing metal salts has been widely reported to reduce membrane fouling by generating more permeable cakes and reducing pore penetration (Benjamin and Lawler 2013, Choi and Dempsey 2004a, Howe and Clark 2006a, Howe et al. 2006, O'Melia 1972, Wiesner et al. 1989b, Wiesner and Laine 1996). Additionally, coagulation pretreatment improves permeate water quality through enhanced removal of contaminants such as DBP precursors, viruses, arsenic, etc. Conventionally, aluminum or iron salts (e.g., alum, ferric sulfate) are used to coagulate water and wastewater (AWWA 2005, Dempsey 2006, Huang

et al. 2009). These metallic salts hydrolyze upon addition to water forming monomeric, dimeric, trimeric, and polynuclear species and solid precipitates depending on the pH (Benjamin and Lawler 2013, Dempsey 2006, Howe and Clark 2002a, Stumm and Morgan 1996, Wiesner and Laine 1996). Destabilization mechanisms by aluminum and iron salts include double layer compression, charge neutralization by adsorption of counter ions, and enmeshment by the precipitates (sweep flocculation)(Benjamin and Lawler 2013, Dempsey 2006).

Electrocoagulation is a promising alternative to conventional coagulation due to its versatility, robustness, amenability to automation, relatively lower consumption of feed water alkalinity, minimal or no handling of corrosive chemicals, and availability of energy optimized skid mountable designs. Here, the coagulant is generated *in situ* through electrochemical dissolution of a sacrificial anode such as aluminum or iron leading to generation of metal hydrolysis products. After a threshold electrolysis time or current density, hydrogen gas evolution by cathodic reduction of water leads to inherent flotation of coagulated flocs. When flotation is utilized along with electrocoagulation, the resulting process is called electroflotation. Critical parameters such as bubble size and flux which affect flotation efficiency can be controlled in electroflotation by varying pH, current density, electrode material, and electrode geometry [4].

Electrocoagulation and electroflotation have been shown to achieve excellent removals of contaminants from municipal and industrial wastewaters when used as a standalone process (Belongia et al. 1999, Cañizares et al. 2005, Cañizares et al. 2006a, Cañizares et al. 2006b, Do and Chen 1994, Lin and Peng 1996, Mameri et al. 1998, Matteson et al. 1995, Mollah et al. 2001, Onstott et al. 1973, Ricordel et al. 2010). However, only a handful of studies have investigated it as a pretreatment option for MF/UF (Bagga et al. 2008b, Ben Sasson and Adin 2010a, Cañizares et al. 2006b, Essadki et al. 2010). Additionally, a majority of researchers have used model waters

of known composition in an attempt to reduce the complexity associated with natural waters (Holt et al. 2002, Li et al. 2012, Shin and Kim 2001, Zhao et al. 2010b). However, such experiments may not provide meaningful results applicable to real-world applications. For example, even though iron electrocoagulation had shown promising results on fouling control during MF/UF of silica suspensions in deionized water (Ben Sasson and Adin 2010b), previous work done by our research group showed that it was ineffective for fouling control during natural water MF (Bagga et al. 2008b).

In this research, aluminum electrochemical pretreatment for fouling control during actual surface water MF was investigated. The first phase of this research (Chapter Two and Chapter Three) investigated fouling and fouling control mechanisms during forward filtration. Here, untreated and pretreated flocs were carefully characterized in terms of particle size, ζ potential, fractal dimensions, chemical composition, and MF cake parameters such as specific cake resistance and compressibility index. Some of the characterization techniques used included optical microscopy, light scattering, electrophoretic mobility measurement, and spectroscopy. X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), and electron microscopy of electrochemically generated solids revealed that the fluffy and gelatinous precipitates mainly consisted of amorphous AI(OH)_{3(s)}. Electrocoagulation controlled fouling through successful destabilization of the raw water colloids generating larger aggregates with greater porosity (lower fractal dimension) hence increasing the permeability of MF cake layer. Sweep flocculation and charge neutralization were identified as the primary particle destabilization mechanisms. XPS analysis revealed effective sorption of potential foulants present in Lake Houston water (e.g., protein-like, carbohydrate-like, siliceous, and humic substances) by electrochemically generated precipitates. Electroflotation improved flux even

better than electrocoagulation, largely due to lower foulant loading transferred to downstream MF, significantly reducing the total cake resistance.

The second phase of the research employed attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) coupled with XPS to analyze physically regenerated membrane surfaces. Foulants on membrane surfaces were characterized to rigorously deduce their contributions to physically irreversible fouling of a modified commercial polyvinylidene fluoride (PVDF) membrane (Chapter Four). Hydrophobic molecules primarily appeared to initiate fouling during microfiltration of untreated raw water since O-H/N-H bands attenuated while C-H bands remained relatively unchanged in FTIR-spectra of membrane surfaces after only one cycle. However, O-H/N-H and symmetric and asymmetric $C(=O)O^{-1}$ stretching bands significantly intensified with continued filtration/regeneration of untreated water showing the importance of hydrophilic molecules and the role of complexation respectively to longer term irreversible fouling. Distinct C-H bands were detected in floated flocs after electrolysis suggesting the sorption and subsequent removal of a substantial portion of the hydrophobic moieties present in Lake Houston water during pretreatment. Consequently, hydrophilic compounds appeared to contribute more to irreversible fouling in pretreated waters throughout the course of filtration as evidenced by significantly more intense O-H bands (than C-H bands) on the regenerated membrane surfaces. Therefore, electroflotation pretreatment reduced accumulation of hydrophobic foulants but simultaneously increased complexation of hydrophilic foulant molecules along with any carried-over aluminum hydroxide precipitates evidenced by increasing Al and O concentrations via XPS and intense C(=O)O⁻ stretching bands in IR spectra.

Chapter Five discusses the results from bench-scale experiments designed to investigate mechanisms of microfiltration (MF) fouling control by aluminum (electro)coagulation pretreatment. Both alum and electrocoagulation reduced membrane fouling but formed highly

compressible cakes compared with untreated Lake Houston water. In all cases, cake specific resistances formed during dead-end MF increased in a power-law fashion with transmembrane pressure. Electrocoagulation produced aggregates of similar size but higher porosity (lower fractal dimension) than alum coagulation thereby reducing the specific resistance at null pressure by an order of magnitude. X-ray diffractometry and electron microscopy revealed that both alum and electrocoagulation generated amorphous and gelatinous Al(OH)₃ flocs, which would have contributed elastically to the compressibility index. Raw water constituents were sorbed effectively on flocs produced by both types of coagulation. However, subtle differences in the chemical state and functionalities of substances taken up by flocs generated via electrolysis and alum addition were measured using high resolution X-ray photoelectron spectroscopy. Compared with alum coagulation, electrocoagulated flocs preferentially accumulated hydrophobic compounds with lower uptake of amides and carboxyl groups that are capable of relatively strong interactions (e.g., hydrogen bonding and complexation). Electrocoagulated flocs can be expected to be more fragile due to their increased branching and porosity coupled to weaker chemical interactions thereby allowing them to compress inelastically to a greater extent due to cake collapse, aggregate breakage and redistribution of fines at higher pressures. Indeed, compressibility indices of cakes formed with electrocoagulation pretreatment were higher than following alum coagulation.

This research resulted in three published journal articles (Gamage and Chellam 2011b, Gamage and Chellam 2013, Gamage et al. 2012) and a fourth is currently in preparation for submission. The first three chapters of this dissertation dedicated to research findings (Chapters Two-Four) are the same as the published journal articles and the fourth chapter is the manuscript that is being written.

1.2. Research Goals and Objectives

The overall goal of my Ph.D. dissertation work was to investigate fouling mechanisms and its control during surface water MF after aluminum electrochemical (i.e., electrocoagulation and electroflotation) and alum coagulation pretreatment. Primary objectives included;

- to empirically quantify flux improvements in forward filtration after aluminum electrocoagulation and electroflotation pretreatment compared with MF of untreated surface water,
- to rigorously elucidate changes in foulant chemical composition during progressive physically irreversible fouling during MF of untreated and pretreated Lake Houston water, and
- to determine the physicochemical basis of cake compressibility following aluminum (electro)chemical pretreatment.

1.3. Dissertation Organization

This dissertation is composed of four chapters dedicated to research findings (Chapters Two-Five) and a chapter discussing the conclusions drawn from the entire study along with recommendations for future research. Chapters 2, 3, and 4 comprise three published journal articles and Chapter 5 is the manuscript currently being written for peer review prior to potential publication.

Chapter Two focuses on evaluating aluminum electrocoagulation pretreatment for surface water MF and delineating the underlying physical mechanisms. Cake filtration was identified as the dominant fouling mechanism in all cases whereas fouling control was found to be optimum at an intermediate coagulant concentration. This work was published in the *Journal of Membrane Science* (Gamage, N. P. and S. Chellam (2011). "Aluminum electrocoagulation pretreatment reduces fouling during surface water microfiltration." **379**(1-2): 97-105).

Chapter Three specifically discusses mechanisms responsible for greater fluxes after electroflotation compared with electrocoagulation pretreatment during Lake Houston water – MF. These findings have also been published already: Gamage, N. P., J. D. Rimer, and S. Chellam (2012). "Improvements in permeate flux by aluminum electroflotation pretreatment during microfiltration of surface water." *Journal of Membrane Science* **411-412**: 45-53.

Chapter Four elucidates fundamental mechanisms responsible for physically irreversible fouling control of a commercial membrane after aluminum electroflotation pretreatment of surface water and this work was published in *Environmental Science & Technology* (Gamage, N. P. and S. Chellam (2013). "Mechanisms of Physically Irreversible Fouling during Surface Water Microfiltration and Mitigation by Aluminum Electroflotation Pretreatment." **48**(2): 1148-1157).

Chapter Five identifies physical and chemical mechanisms underlying cake compressibility during MF of untreated and pretreated (electrocoagulation and alum coagulation) Lake Houston water. This work will be submitted for peer-review in the near future.

From Chapter Two-Four, all chapters are presented in the same format as the published article and each chapter begins with a brief introduction followed by experimental section, results and discussion, and finally the relevant conclusions. Same format is followed in Chapter Five, the written manuscript to be submitted for peer review.

Chapter Two. Aluminum Electrocoagulation Pretreatment Reduces Fouling during Surface Water Microfiltration

2.1. Introduction

The greater Houston, Texas area is one of the fastest growing regions in the United States, increasing in population by 25% between 1990 and 2000 and is estimated to grow by another 45% by the year 2030. More water purification facilities are being designed and built to meet the increasing demands of the growing population. Of particular importance to the process of planning new drinking water treatment plants is that over 12,000 km² of land in and around the City of Houston, Texas has subsided more than 0.5 feet, with some areas subsiding more than 10 feet primarily due to excessive groundwater extraction. Subsidence-induced lowering of the land surface elevation has increased the frequency and severity of flooding, damaged the built-infrastructure including industrial and residential buildings as well as roads and bridges, and reduced coverage of sensitive wetland ecosystems and marshes (Coplin and Galloway 1999). To mitigate these adverse effects, the City of Houston has been mandated to meet the entire water demand only using surface water supplies by the year 2030.

Microfiltration (MF) is an attractive choice for purifying surface waters largely because it is capable of very high removals of protozoa including *Giardia* and *Cryptosporidium*, bacteria, and other microbial indicators. Hydrolyzing metal salts such as ferric chloride or aluminum sulfate are often added to feed waters to reduce microfilter fouling (Howe and Clark 2006b, Wiesner et al. 1989b, Wiesner and Laîné 1996). Electrocoagulation is an attractive alternative to conventional chemical coagulation since it (i) reduces the direct handling of corrosive chemicals, (ii) does not consume the natural buffering capacity (alkalinity) of the water, (iii) is thought to produce lower amounts of sludge, and (iv) can be easily employed in portable water purification units (Holt et al. 2005, Mollah et al. 2004). Electrocoagulation has been shown to be successful for the removal of organic compounds (Cañizares et al. 2006a, Jiang et al. 2002), heavy metals (Mouedhen et al. 2008, Yang and Tsai 2006), anions (Mameri et al. 1998, Shen et al. 2003), microorganisms (Zhu et al. 2005), and turbidity (Holt et al. 2002) from municipal and industrial wastewaters as well as contaminated drinking water supplies. However, its suitability for MF pretreatment is only just beginning to be evaluated (Bagga et al. 2008a, Ben Sasson and Adin 2010a, Timmes et al. 2009, 2010).

Generation of soluble ferrous ions and accumulation of colloidal precipitates on electrodes suggests disadvantages of iron electrocoagulation pretreatment for micro- and ultrafiltration of industrial-, surface-, and saline waters (Bagga et al. 2008a, Ben Sasson and Adin 2010b, Timmes et al. 2009, 2010). Therefore, it was hypothesized that electrocoagulation performance would be improved using the other common metal-ion coagulant, namely aluminum. Limited data available from synthetic water experiments suggests that substantial energy conservation is possible from aluminum electrocoagulation pretreatment to dead-end MF (Ben Sasson and Adin 2010a). The specific objectives of this research were to determine electrocoagulation and MF mechanisms by varying operating conditions such as electrocoagulation and MF mechanisms by varying operating conditions such as representative surface water source. Morphological aspects of aluminum precipitates were probed using X-ray diffraction. Optical microscopy and an electrical sensing zone device were both employed to characterize floc size distributions prior to constant pressure MF.

2.2. Experimental Work

2.2.1. Source water

A water sample collected from the Lake Houston Canal at the City of Houston's East

Water Purification Plant on December 14, 2009 served as the basis for all data reported herein. This sample was stored at 4 °C in a walk-in temperature controlled room to reduce potential deteriorations in water quality. It was regularly monitored for dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm and 1 cm path length (UV₂₅₄), turbidity, pH, conductivity, and total and calcium hardness. Time series plots of the various water quality parameters monitored are summarized in Figure A7.1 of the Appendix. This particular sample could be characterized as being near neutral (pH 7.4±0.14), turbid (24.9±2.4 NTU), soft (total hardness 41.5±1.2 mg/L as $CaCO_3$ and calcium hardness 34.0±1.2 mg/L as $CaCO_3$), with low alkalinity (39.4±1.6 mg/L as CaCO₃), low conductivity (169.7 \pm 2.68 μ S/cm), and having high natural organic matter concentrations (DOC 7.97±0.50 mg/L and UV₂₅₄ 0.345±0.018 cm⁻¹). The values given here represent the average and the standard deviation for 31 to 45 analyses of the single water sample conducted over a 9-month time frame between December 18, 2009 and September 3, 2010 during which all experiments were performed. The low coefficients of variation associated with each parameter also demonstrate the integrity of our sample storage and the high reproducibility of our analytical techniques. An electron micrograph (see §2.2.5) showing the heterogeneous nature of natural colloidal materials present in our surface water sample is given in Figure A7.2 of the Appendix.

2.2.2. Electrocoagulation

Each experiment consisted of electrochemically coagulating 450 mL of water at room temperature in a cylindrical Perspex cell at pH values of 6.4 or 7.5 maintained to a precision of ± 0.2 pH units. A single 15 cm long aluminum rod (Puratronic grade, 99.9965% as Al, Alfa Aesar) served as the anode, which was surrounded by a porous cylindrical 316-stainless steel cathode. The anodic active surface area was 12.5 cm² corresponding to 10 cm of the rod being submerged in water. As predicted by Faraday's Law (Equation 1), different Al concentrations can

be generated by either varying the current or the generation time:

$$m = \frac{26.98It}{zF},$$
 (1)

where m is the mass in grams of Al generated at a specific current (I, ampere) over a time interval (t, second), z is the number of electrons transferred per Al atom, 26.98 g mol⁻¹ is the atomic weight of Al, and F is Faraday's constant (96,486 C eq⁻¹). In our experiments, the current density was kept constant at 20 mA/cm² and different Al concentrations in the range of 2-30 mg/L were generated by operating the unit for different generation times in batch mode.

Electrocoagulation was carried out in two steps; electrolysis and flocculation. It is emphasized that a separate sedimentation step was not employed in accordance with the most common application of coagulation pretreatment for MF during water/wastewater treatment. During electrolysis, the solution was rapidly mixed with a magnetic stirrer to enhance mass transfer of aluminum away from the anode. The suspension was then slowly mixed for 2 minutes to flocculate the destabilized particles. Since deposit accumulation around the anode can cause problems with electrochemical dissolution, the anode was mechanically scrubbed with a waterproof silicon paper sanding sheet (100 Grit, McMaster-Carr) before each experiment in order to maintain the aluminum generation efficiency. As reported earlier (Chen et al. 2000, Mouedhen et al. 2008), electrocoagulation increased the water pH especially given the low buffering capacity of the source water. Empirically, we observed a greater pH increase with longer electrocoagulation duration. For example, when the initial source water pH was 7.5, the pH after electrocoagulation increased to 7.8 for 10 mg/L Al dose and 8.0 for 30 mg/L Al dose.

Water samples were collected before and after electrocoagulation and acidified to pH 2 using 11.5 N HCl (final concentration 2%) to redissolve aluminum precipitates before instrumental analysis. Total aluminum concentrations were analyzed using flame atomic
absorption spectroscopy (Flame AA-AAnalyst 300, Perkin-Elmer) according to Standard Method 3111. The instrument was calibrated in the range 0 – 50 mg/L using 1,000 mg/L AI stock solution with 2% HCI (High Purity Standards) prior to each set of measurements. Given the importance of accurate aluminum measurements to this study, concentrations covering the entire range of dosages were independently verified using inductively coupled plasma – mass spectrometry (Figure A7.3 in the Appendix). The two analytical techniques agreed within 95% confidence demonstrating the accuracy of aluminum measurements reported in this manuscript.

2.2.3. Microfiltration

Constant pressure, unstirred dead-end filtration experiments were conducted using a commercially available cell, with 4.1 cm² of effective filtration area (Model 8010, Millipore). Modified PVDF membranes rated at 0.22 μ m (GVWP02500, Millipore) were used. The system was pressurized by compressed air and the feed pressure was maintained at predetermined values in the range 13-166 kPa (2-24 psig) using a precision regulator (PRG101-60, Omega). The length of tubing and number of fittings were kept to a minimum in order to more accurately monitor the time trace of permeate flux. 100 mL of ultrapure water was passed through the system first to rinse the membrane of any preservatives and evaluate its resistance prior to filtering 150 mL of the electrocoagulated suspension. The Darcy resistance (R_m) of the membranes employed in this study was $5.38\pm0.42 \times 10^{10}$ m⁻¹.

A transducer (PX303-050G5V, Omega) and a digital balance (Ohaus Navigator N1H110, Fisher Scientific) were used to monitor the pressure and cumulative mass of permeate water respectively during filtration. Data were acquired at a frequency of 1 Hz for the first 2.5 cm³/cm², 0.2 Hz between 2.5 and 5 cm³/cm², and 0.1 Hz for > 5 cm³/cm² of water filtered per area of membrane using a computerized data acquisition system programmed in LabVIEW (National Instruments). The cumulative permeate volume per unit membrane area data

acquired over time was exponentially smoothed using a damping factor of 0.3 prior to numerical differentiation to obtain the instantaneous flux. Following filtration, the cake was weighed after drying to a constant weight for 16 h at 35 °C.

Approximately 20% of the experiments at different pH, coagulant dosage, and pressures were repeated. Statistical analysis of instantaneous relative flux values and cake specific resistances from duplicate experiments revealed no differences at 95% confidence (see Figures A7.4 and A7.5 in the Appendix). Hence, all our laboratory protocols related to coagulation, flocculation, and MF were consistent and highly reproducible thereby allowing a quantitative comparison of results generated over the entire duration of experimentation.

2.2.4. Floc size distributions and zeta potentials

Effective size distributions of coagulated suspensions and colloids in the raw water were obtained using an electrical sensing zone device (Multisizer III, Beckman Coulter) within 30 minutes of electrocoagulation. Particles in the 2-240 µm size range were detected using 100 µm and 400 µm diameter apertures, which were calibrated using highly monodispersed NIST-certified polystyrene latex beads of size 10 µm and 43 µm respectively. Particle size distributions were obtained with a current of 3,200 µA and a gain of 1 after 100-fold dilution with prefiltered 2% NaCl solution containing 20% glycerin. Adding glycerin increased the viscosity of the background electrolyte thereby reducing clogging and floc breakage when flocs passed through the aperture. 1 mL of the suspension was drawn and each run was completed in 20 s. The entire suspension was gently stirred during the analysis period in order to avoid settling. Resulting size distributions from the two different apertures were merged using MULTISIZER/Z2 AccuComp[®] software provided with the instrument. The average of triplicate analysis of each sample is reported herein.

The electrophoretic mobility of electrocoagulated suspensions was measured using the

electrophoretic light scattering technique (Nicomp 380 ZLS, Particle Sizing Systems, Santa Barbara, CA). A He-Ne laser of wavelength 632.8 nm, an electrode spacing of 0.4 cm, and a field strength of 10 V/cm were employed for all measurements. Colloidal silica suspensions (Snowtex 50, Nissan Chemicals, Houston, TX) were used for calibration. The Smoluchowski equation was used to convert electrophoretic mobility to zeta potential. Each sample was run in two replicates of 60 seconds duration each.

2.2.5. Microscopy

Scanning electron micrographs (SEMs) of clean and fouled membranes were obtained with a field emission scanning electron microscope (LEO 1525, Carl Zeiss) after sputter coating the oven dried samples (16 h, 35 °C) with a 10 nm layer of gold. Electron Dispersive Spectra (EDS) of sputter coated filter cakes were acquired with a 15 keV primary beam voltage on a Jeol JSM 6330F microprobe using an Oxford Instruments ISIS 300 EDS detector.

Flocs were also observed under an optical microscope (CTR4000 Leica Microsystems Wetzlar GmbH, Germany) to visualize their sizes and shapes. 0.2 mL of electrocoagulated water samples were placed on glass slides using a manual pipette where the tip was cut to 5 mm diameter and excess water was carefully removed with a tissue paper. Phase contrast images were obtained using a 10x objective with 1.6x enhanced magnification. RGB images with a 1280 x 1024 pixels resolution were obtained with high speed digital camera (S-PRI, AOS Technologies AG, Switzerland) using AOS Imaging Studio (v. 3.2.5) software. The microscope was calibrated using a graduated microscale where the scale for images obtained under the aforementioned settings was 1.2±0.2 μm/pix. Images were processed and particle sizes analyzed using MATLAB R2009b software with the image processing toolbox. The RGB image was converted to a 256 grey level image after image enhancement (brightness, contrast adjustment and histogram-based thresholding was applied to differentiate dark and bright

pixels in order to differentiate the background from the particles. An example is provided in Figure A7.4 of the Appendix. The connected components in the resulting binary image were labeled and the inbuilt function *regionprops* was used to calculate the equivalent diameters of the connected regions. Size distributions were calculated using the equivalent diameter data obtained in terms of pixels and converted to µm later.

2.2.6. Powder X-ray diffractometry

The polymorphs of precipitates produced during aluminum electrocoagulation were identified examined by X-ray diffraction (XRD, Siemens D5000) equipped with a graphite monochromator. The flocs were collected after filtration and dried at ambient temperature for 1 day because drying at higher temperatures can lead to experimental artifacts such as increased crystallinity (Roček et al. 1991). The flocs were then powdered and dispersed in isopropyl alcohol. The alcohol was then evaporated in order to make a thin uniform coat on the zero background quartz sample holder. Diffraction patterns were collected using CuK α radiation (1.54056 Å) at 40 kV and 30 mA in the 2 Θ scan range from 5° to 60° with steps of 0.04° 2 Θ /s. A quartz standard was measured initially for calibration purposes. The Joint Committee for Powder Diffraction Studies (JCPDS) database was used to interpret the diffraction patterns and identify the peaks.

2.3. Results and Discussion

2.3.1. Aluminum generation accurately follows Faraday's law with 3 electron transfer

Aluminum concentrations from multiple experiments performed on different days corresponding to various current passage times are shown in Figure 2.1. Note that the straight line in Figure 2.1 is the purely theoretical prediction using Faraday's law obtained for a three electron transfer (z = 3 in Equation 1). As observed, experimental data agree closely with Faraday's law predictions, the relative percent difference varying between only 1 to 6% for the entire range of concentrations employed. The extremely accurate predictions of Faraday's law demonstrate the *in situ* electrochemical generation of aluminum cations with the characteristic +3 oxidation state of group 13 elements at near 100% efficiency.



Figure 2.1. Near 100% efficiency of aluminum (Al^{3+}) generation during electrocoagulation of Lake Houston water.

The 3-electron transfer inferred from Figure 2.1 suggests that the following major electrochemical reactions:

Anode:	$AI^{0}_{(s)} = AI^{3+}_{(aq)} + 3e^{-},$
Hydrolysis:	$AI_{(aq)}^{3+} + 3H_2O_{(I)} = AI(OH)_{3(s)} + 3H_{(aq)}^{+}$
Cathode:	$3H_2O_{(I)} + 3e^- = 3OH_{(aq)} + 1.5H_{2(g)}$, and
Overall:	$AI_{(s)}^{0} + 3H_2O_{(I)} = AI(OH)_{3(s)} + 1.5H_{2(g)}.$

Hydrolysis of Al³⁺ cations produces protons reducing the pH in the anodic microenvironment. Note that hydroxide anions generated at the cathode neutralize these protons in the bulk solution thereby preserving the natural buffering capacity of the source water. This is in contrast to conventional chemical coagulation wherein iron or aluminum hydrolysis consumes alkalinity (Brønsted acid behavior) necessitating external addition of a base to neutralize protons released. This constitutes a substantial operational advantage for

electrocoagulation especially for treating low alkalinity waters such as Lake Houston. Other studies have attributed large differences between Faraday's law predictions of electrolytic Al generation and experimental values to pH changes in the electrode microenvironments or electrode corrosion (Chen et al. 2000, Mouedhen et al. 2008, Shen et al. 2003).

Electrochemically generated AI^{3+} ions can also produce other charged monomeric, dimeric, and polymeric hydroxo-metal complexes such as $AI(OH)^{2+}$, $AI(OH)_{2}^{+}$, $AI(OH)_{4}^{-}$, $[AI_2(OH)_2]^{4+}$, $[AI_3(OH)_4]^{5+}$, $[AI_{13}O_4(OH)_{24}]^{7+}$, etc. that are surface-active (Duan and Gregory 2003, O'Melia 1972). The atomic structure of $AI(OH)_3$ precipitates was probed using XRD as described next.

2.3.2. Electrocoagulation produces amorphous aluminum hydroxide precipitates

Aluminum polymorphs formed *in situ* depend on electrode materials and source water composition (Emamjomeh and Sivakumar 2009a, Gomes et al. 2007). Hence, X-ray diffractograms of electrocoagulated samples of natural water were obtained in this research. As summarized in Figure 2.2 diffractograms did not show any strong peaks demonstrating the absence of any crystalline precipitates. This is similar to fresh precipitates obtained during alum coagulation of surface water (Berkowitz et al. 2005) and during electrocoagulation of textile wastewaters (Mollah et al. 2010). Note that the two clearly visible peaks correspond to silica present in the natural water, which was verified by EDS. Weak signals corresponding to the principal peak of boehmite (020 plane) were discerned suggesting the primary species was amorphous Al(OH)₃ but that small amounts of the oxyhydroxide AlO(OH) were also present. Residual water intercalated between the boehmite layers as well as natural organic matter and other constituents disallowed the resolution of the secondary AlO(OH) peaks from the background. Additionally, the weak signal was shifted approximately 1° 20 towards smaller angles potentially due to high interlayer spacing caused by the lack of long range order and

structural distortion of boehmite. Also as seen in Figure 2.2, the diffractogram of electrocoagulated aluminum precipitates in ultrapure water showed very shallow and broad principal and secondary peaks, which were stronger than those observed with natural water. Hence, Al(OH)₃ precipitates were amorphous in nature and small amounts of very fine boehmite grains were present.



Figure 2.2. XRD analysis of flocs formed by electrocoagulation of natural and ultrapure waters at different aluminum dosages (left). Scanning electron micrographs of Al(OH)₃ precipitates formed in ultrapure water are shown on the top middle and right and those formed in natural water at 15 mg/L Al are shown in the bottom middle and right.

Electron micrographs of Al(OH)₃ precipitates formed in ultrapure and natural waters support this observation since no order or habit was discerned (see Figure 2.2). In all cases, the aggregates appeared to be largely amorphous and gelatinous of various sizes and shapes. The formation of such poorly crystalline precipitates in the presence of natural organic matter is consistent with literature reports of competition of organic acids with hydroxyl ions to form polymorphic amorphous Al(OH)₃ (Masion et al. 1994, Violante and Huang 1985). The slightly stronger signals obtained in ultrapure water suggests the role of natural organic matter (NOM) and other natural water chemical constituents in influencing aluminum precipitation or in adding to the background signal. Note that we dried our samples at room temperature to more closely capture the actual morphology and structure of the fresh precipitates. Drying at higher temperatures (e.g., 105 °C) can increase the order forming crystalline minerals such as bayerite (Ricordel et al. 2010).

2.3.3. Effect of aluminum dosage on fouling

The relative permeate flux increased with aluminum dosage up to an intermediate value (15-20 mg/L for pH 7.5 and 10 mg/L for pH 6.4) and then reduced when the dose was increased further as shown in Figure 2.3 for a low applied pressure of 13.8 kPa. In other words, fouling was alleviated only up to an intermediate value of aluminum dosage beyond which higher coagulant dosages worsened fouling. Similar observations have been reported for crossflow MF of iron electrocoagulated kaolin suspensions (Al-Malack et al. 2004) as well as dead-end MF of alum-coagulated humic acids (Wang et al. 2010) and aluminum electrocoagulated silica suspensions (Ben Sasson and Adin 2010a). The variations in relative flux with aluminum concentrations were less pronounced at higher pressures, which was attributed to cake compression (see §2.3.6).



Figure 2.3. Improvements in relative permeate flux only up to an intermediate value of aluminum dosage at a constant transmembrane pressure for both pH values investigated. The symbols denote experimental data and the curves are model fits to Equation 2.

Excellent fits of the cumulative volume filtered (V) to the cake filtration model (Equation

²⁾ were obtained as seen in Figure 2.3,

$$\frac{t}{V/A_{m}} = \frac{\mu R_{m}}{\Delta P} + \frac{\mu \alpha^{*} c_{b}}{2\Delta P} \left(\frac{V}{A_{m}}\right), \quad (2)$$

where A_m is the membrane area, μ is the absolute water viscosity, cb is the bulk solids concentration, α^* is the specific cake resistance on a mass basis, and ΔP is the transmembrane pressure. Also a thick cake layer of Al(OH)₃ flocs which appeared to have completely enveloped all particles in the raw water can be seen in the electron micrographs on the bottom right in Figure 2.2. Excellent model fits and visual observations therefore demonstrate the predominant role of surface deposits on flux decline and that cake filtration was the governing fouling mechanism for the entire range of experimental parameters investigated. The absence of a distinct pore blocking phase is probably due to the higher particle concentration in the current water sample compared with our earlier work (Bagga et al. 2008a) evidenced by doubling of the feed water turbidity (~25 NTU versus 13 NTU) coupled with the more efficient precipitation of Al(OH)₃ (rather than soluble Fe²⁺ generation).



Figure 2.4. Effects of increasing aluminum electrocoagulant dosage: declining specific resistances at a fixed transmembrane pressure of 83 kPa and increasing total mass of solids in the feed water (inset).

As summarized in Figure 2.4, specific cake resistances decreased rapidly with coagulant addition at a fixed transmembrane pressure; the raw water forming the least permeable deposits. Further, as can be expected, higher aluminum concentrations increased the total cake mass for both pH values investigated as shown in the inset of Figure 2.4. The conflicting effects of increasing aluminum dosage which on one hand decreased specific cake resistance but simultaneously augmented the total loading of colloidal foulants caused the cumulative cake resistance to be minimum at an intermediate aluminum concentration (the optimal dose). Floc properties including size distributions and zeta potential were measured to mechanistically understand underlying causes of the observed fouling profiles and trends in the cake resistance as described below.

2.3.4. Characteristics of flocs formed at different aluminum dosages

Volume-based floc size distributions measured using an electrical sensing zone device (Coulter Counter) following electrocoagulation at various aluminum dosages at pH 6.4 are shown in Figure 2.5.



Figure 2.5. Particle size distributions at different aluminum dosages obtained using an electrical sensing zone device. The inset summarizes volume-averaged mean diameters obtained from the Coulter Counter and digital analysis of optical micrographs.

As expected, the cumulative floc volume increased monotonically with aluminum dosage mirroring the observed trend in mass reported in the inset of Figure 2.4. Also as can be seen in Figure 2.5, the volume distributions shifted to the left corresponding to smaller sizes as the coagulant dose increased progressively beyond 10 (optimal dose) to 15, 20, and 30 mg/L. Note that size distributions for lower dosages (0, 2, and 5 mg/L) aren't discerned due to the significantly lower floc volumes generated. Arithmetic average diameters calculated from these data increased from the raw water (5.5 μ m) to the optimal dose of 10 mg/L (13.8 μ m) but decreased as more aluminum was added (5.1 μ m at 30 mg/L Al) indicating that larger flocs were breaking up as they passed through the instrument's aperture. Optical microscopy was undertaken to avoid this potential artifact and better determine the actual floc size (see Figure 2.6). As can be seen qualitatively in Figure 2.6, which shows representative images for the raw water and electrocoagulated suspensions, both particle size and concentration appeared to increase with aluminum concentration. These images were also used to digitally calculate volume-weighted average particle sizes which are summarized in the inset of Figure 2.5. In contrast to the average diameters calculated with the electrical sensing zone instrument, sizes calculated from digital analysis of microscopic images increased monotonically with aluminum dosage. Further, the average diameter from image analysis was always significantly greater than that measured with the Coulter Counter (e.g., 146.1 µm and 13.8 µm respectively at 10 mg Al/L). Both these observations are consistent with our earlier hypothesis of floc breakage while passing through the aperture of the electrical sensing zone device. Hence, formation of larger particles during electrocoagulation pretreatment as more aluminum was added at a fixed pH reduces specific cake resistances during constant pressure MF.



Figure 2.6. Optical images of flocs formed by electrocoagulation at different aluminum dosages.

As summarized in Figure 2.7, zeta potentials of flocs increased (\rightarrow 0) with aluminum dose for a constant pH similar to earlier reports with electro- and chemical coagulation using alum and polyaluminum chloride (Holt et al. 2002, Zhao et al. 2010a). Adsorption of hydrolyzed aluminum species onto natural colloidal material will increase the zeta potential of negatively charged flocs (Duan and Gregory 2003, O'Melia 1972). Greater degree of protonation of adsorbed NOM functional groups at lower pH resulted in less negative zeta potentials at pH 6.4 compared with 7.5. The higher rate of surface charge neutralization with increasing aluminum dosage at pH 6.4 is also consistent with the predominant positively charged species at that pH (Al(OH)₂⁺) whereas at 7.5 the dominant species is negatively charged (Al(OH)₄⁻). Interestingly, negative floc zeta potentials were measured at the optimal coagulant dosage for fouling control at both pH values. Hence, charge neutralization wasn't the major destabilization mechanism but only played a secondary role to enmeshment and sweep flocculation during electrocoagulation. In contrast, alum destabilized humic acids in synthetic waters through complexation and charge neutralization resulting in lowest fouling when the ζ potential was ~ 0 mV (Wang et al. 2010). This demonstrates different destabilization mechanisms in natural and synthetic waters possibly dependant on the method of aluminum addition as well as colloid and NOM composition and concentration. Importantly, the pH value of 6.4 also approximately corresponds to the minimum aluminum solubility and the optimum pH for alum coagulation (O'Melia 1972).



Figure 2.7. Progressive charge neutralization (ζ potential \rightarrow 0) by increasing aluminum dosage at pH 6.4 and 7.5.

2.3.5. Fouling worsened with increasing transmembrane pressures

As reported earlier in other MF studies e.g., (Belfort et al. 1994), fouling worsened at higher pressures (or initial fluxes) at fixed pH and aluminum dosage in our experiments. These results are summarized in Figure 2.8 which depicts relative flux profiles corresponding to the optimal aluminum dosage for both pH values investigated.



Figure 2.8. Evidence of cake compaction with lower normalized fluxes observed with increasing pressures at fixed pH and aluminum dose.

An inverse relationship between normalized fluxes and filtration pressures is consistent with cake compaction, with lower permeabilities of surface deposits measured at higher pressures. As shown in Figure 2.9, specific cake resistances increased in a power law manner with pressure for a given aluminum dose,

$$\alpha^* = \alpha_o^* (\Delta P)^n, \qquad (3)$$

where α_{o}^{*} is specific resistance of an unstressed cake the and n is the compressibility index.

Compressibility indices generally increased with aluminum dosage increasing from 0.39 for the raw water to 0.49, 0.61, and 0.68 for aluminum dosages of 5, 10, and 15 mg/L respectively at pH 6.4 (Figure 2.9). A similar trend was also observed at pH 7.5 for electrocoagulated suspensions with compressibility indices increasing from 0.32 to 0.68 as aluminum dose increased from 2 to 20 mg/L. This suggests a higher degree of transport of fines, floc breakage, and colloid rearrangement as pressure increased, all of which contributed to the overall cake compaction.



Figure 2.9. Power law compressibility of colloidal deposits formed on the membrane surface at different coagulant dosages and pH.

As expected, the raw water compressibility index was similar at pH 6.4 and 7.5, but higher than low aluminum doses at 7.5. Compressibility indices in this study varied between 0.3 and 0.8, which is the same range measured during iron electrocoagulation and other natural waters (Bagga et al. 2008a, Sørensen and Sorensen 1997, Tiller et al. 1987c) and cakes formed in this research can be classified as being moderately to highly compactible. Cake compaction will induce more rapid fouling (pressure increase rate) during constant flux MF of coagulated suspensions as is often practiced in full-scale systems (Chellam and Jacangelo 1998b). The rapid pressure build-up can only be partially compensated by more frequent backwashing or chemically-enhanced backwashes. Therefore, constant flux operation can be expected to eventually reduce chemical cleaning intervals increasing both capital costs (additional membrane area) and operational costs (more cleaning chemicals). Increased fouling in the constant flux mode has already been reported in the literature even for incompressible silica particles and untreated surface waters (Chellam and Jacangelo 1998b, Tarabara et al. 2002). This strongly suggests the benefits of operating microfilters at constant pressure following electrocoagulation pretreatment especially for higher coagulant concentrations, which correspond to higher compressibility indices. This is also expected to apply qualitatively to membrane bioreactors since microbial flocs are also compressible. However, since microorganisms exhibit different compression behavior than inorganic particles and flocs (straight line compared with power-law), separate experiments are necessary to quantitatively assess bioreactor fouling under constant flux versus constant pressure operation.

2.3.6. Higher fluxes were observed at a lower feed water pH

For a given coagulant dosage, fouling was substantially reduced at the lower pH investigated at a low transmembrane pressure as shown in Figure 2.10. Improved fluxes at pH 6.4 compared with pH 7.5 were attributed to the formation of more permeable cakes near the pH for minimum aluminum solubility. For example, for the data presented in Figure 2.10, the specific resistance at 13.8 kPa decreased from 2.9 x 10¹³ m/kg to 9.4 x 10¹² m/kg as the pH was reduced from 7.5 to 6.4. The lower pH also corresponds to more efficient charge neutralization by Al(OH)²⁺. Cake compaction at higher filtration pressures manifests as very similar relative flux profiles regardless of the pH (see inset of Figure 2.10). Note that these results are in contrast to iron electrocoagulation where sharper fouling was measured at pH 6.4 due to electrolytic



generation of soluble Fe^{2+} that formed smaller flocs (Bagga et al. 2008a).

Figure 2.10. Improved normalized fluxes at pH 6.4 compared with pH 7.5 at a low transmembrane pressure. At higher pressures, the pH effect is negligible (inset).

2.4. Conclusions

Switching the electrocoagulant to aluminum reduced fouling substantially (unlike iron (Bagga et al. 2008a)) suggesting its potential suitability for water/wastewater treatment. Since our results are based on short-term bench-scale experiments under idealized conditions, long-term testing larger scale at site-specific conditions are necessary before the suitability for electrocoagulation for full-scale applications can be conclusively established. In the range of experimental conditions investigated, a combination of lower pH, low pressure, and intermediate aluminum concentrations were optimal for fouling mitigation during electrocoagulation-MF. Fouling was reduced most for an aluminum dosage corresponding to the lowest cumulative cake resistance where the conflicting effects of creating larger flocs (lower specific resistance) and adding more mass of foulants (higher total resistance) were balanced. Cake compaction increased fouling with pressure suggesting the merits of constant pressure operation over constant flux mode as is currently practiced in full-scale MF systems.

Only short-range order was discerned in X-ray diffraction patterns demonstrating precipitation of amorphous Al(OH)₃ during electrocoagulation. Oxide film formation on the electrode and its subsequent corrosion is an important issue related to electrocoagulation (Mouedhen et al. 2008), which to date can only be evaluated only through site-specific long-term tests. Electrode passivation, pitting, and chemical dissolution have been implicated in variations in aluminum generation efficiency between ~100% to even > 200% (Canizares et al. 2005, Chen et al. 2000, Mameri et al. 1998, Mouedhen et al. 2008, Shen et al. 2003). Since the kinetics of these phenomena cannot be theoretically predicted for natural waters, empirical evaluation of the electrocoagulation-MF process is strongly recommended. It is again emphasized that bench-scale results summarized herein need to be verified at larger-scale to obtain engineering design parameters.

Fine hydrogen bubbles released from the cathode (and in some cases oxygen evolution from water splitting at high anode potential) could potentially influence the floc morphology and induce flotation (Gao et al. 2010, Jiang et al. 2002). We observed partial flotation of flocs for certain experiments, which we empirically hypothesize to become more evident at higher current densities or current passage times (corresponding to higher aluminum concentrations and longer durations of bubble formation).

Chapter Three. Improvements in Permeate Flux by Aluminum Electroflotation Pretreatment during Microfiltration of Surface Water

3.1. Introduction

Performance reductions and associated cost increases caused by membrane fouling can often be successfully combated by pretreating (or conditioning) the feed water. For example, fouling of microfiltration (MF) and ultrafiltration (UF) membranes during drinking water purification is commonly reduced by chemical coagulation pretreatment (Howe and Clark 2006b, Wiesner et al. 1989b, Wiesner and Laine 1996). This provides the additional benefit of improving filtered water quality by controlling disinfection by-product precursors and viruses, which are not removed to a significant extent by MF alone (Randtke 1999, Shirasaki et al. 2009, Zhu et al. 2005). Recent advances in electrochemical technologies have generated much interest in evaluating them as alternatives to conventional coagulants such as alum or ferric chloride (Canizares et al. 2005, Chen 2004, Holt et al. 2005, Mollah et al. 2001). During electrochemical treatment, current is passed through a sacrificial anode to dissolve Al or Fe ions in situ. This has been reported to achieve excellent contaminant removals from municipal and industrial wastewaters when used as a stand-alone process (Chen 2004, Chen et al. 2002b, Emamjomeh and Sivakumar 2009b, Holt et al. 2005, Mollah et al. 2001). Moreover, a limited number of studies have evaluated it in combination with MF/UF for drinking water treatment where AI performed better than Fe (Bagga et al. 2008b, Ben Sasson and Adin 2010a, Gamage and Chellam 2011b, Timmes et al. 2009). When the entire electrolyzed suspension is directly filtered (without intermediate sedimentation) the process is referred to as electrocoagulation (or electroflocculation) (Ben Sasson and Adin 2010a, Chen 2004). It is emphasized that electrocoagulation pretreatment increases the mass loading on the membrane because of coagulant precipitation (compared with untreated raw water).

Along with anodic dissolution of the coagulant, hydrogen bubbles are released from the cathode due to water splitting (Canizares et al. 2005, Chen 2004, Holt et al. 2005, Mollah et al. 2001). Floc flotation caused by gas evolution during electrochemical treatment of industrial and metallurgical feed waters and wastewaters has been termed electroflotation (Chen 2004, Ricordel et al. 2010, Sarkar et al. 2010). We have also reported flotation of coagulated and flocculated colloids for longer duration of current passage and associated higher electrocoagulant concentrations during electrolysis of municipal drinking water supplies (Gamage and Chellam 2011b). The floating layer can be easily skimmed off the top without adding a separate step in the treatment train. In other words, electroflotation reduces the colloid concentration fed to any downstream process without increasing treatment train complexity, footprint, or cost. Moreover, external air injection into a submerged membrane unit has been shown to reduce membrane fouling by a combination of floc flotation and membrane scouring (Lazaridis et al. 2004, Matis et al. 2005). We therefore hypothesize that it would be feasible to use electroflotation pretreatment to reduce fouling in a hybrid electroflotation-MF process by decreasing the solids concentration in the MF feed water. It should be noted that electroflotation in this paper involves both coagulation and flotation occurring in a single unit. Other process combinations wherein electroflotation is performed separately after electrocoagulation using a different electrode combination or as a standalone process using inert anodes that do not generate coagulants can also be designed (Chen et al. 2002b, Lei and Maekawa 2007, Manohar et al. 1982).

The primary objective of this research is to quantify improvements in microfilter flux following electroflotation of surface water. Lake Houston was used as a representative surface

water source since we are interested in developing alternative treatment processes to meet the increasing demands associated with population growth and mandates to eliminate groundwater usage in the greater Houston area (Coplin and Galloway 1999). Electroflotation was compared with raw water MF (i.e., no pretreatment) and electrocoagulation pretreatment in the dead-end mode in a range of Al dosages and pressures at pH 6.4. Experimental flux profiles were interpreted using cake filtration theory as well as the fractal dimension, average size, zeta potential, and elemental composition of the aggregates in the microfilter feed water.

3.2. Experimental Methods

3.2.1. Source water quality

Water was collected from the Lake Houston Canal at the City of Houston's East Water Purification Plant on January 25, 2011 and was stored at 4 °C. This sample was near neutral (pH 7.6±0.19), moderately turbid (14.7±1.5 NTU), soft (total hardness 51±3 mg/L as CaCO₃ and calcium hardness 48±3 mg/L as CaCO₃), with buffering capacity (alkalinity) of 71±2 mg/L as CaCO₃, low conductivity (328±13 μ S/cm), and having moderate natural organic matter (NOM) concentrations (dissolved organic carbon 4.9±0.5 mg/L and UV₂₅₄ at 1 cm path length 0.143±0.005 cm⁻¹). These values represent 25 to 30 measurements of the stored raw water over the period of experimentation between January 25, 2011 and September 15, 2011.

3.2.2. Electrocoagulation, electroflotation, and microfiltration

The cylindrical Perspex electrochemical cell consisted of a single 15 cm long anode (Puratronic, 99.9965% as Al, Alfa Aesar) inside a porous cylindrical 316-stainless steel cathode. This same anode-cathode combination was employed for both electrocoagulation and electroflotation experiments. Lake Houston water (450 mL) was electrochemically treated with 10 cm of the rod being submerged corresponding to an active surface area of 17.27 cm². Different concentrations of aluminum (2-30 mg/L) were quantitatively dissolved in accordance with Faraday's law using a constant current density of 20 mA/cm² while varying the generation times (39 – 580 s) in batch mode (Gamage and Chellam 2011b). The suspension was stirred thoroughly during electrolysis to simulate rapid mixing. Flocculation was performed by slow mixing for two minutes. During electroflotation, the treated water was drained out from the bottom of the electrolysis cell avoiding the carryover of floating flocs to downstream microfiltration. In contrast, in electrocoagulation the entire electrochemically treated suspension was mixed well and transferred to the microfiltration feed tank (direct microfiltration). It is emphasized that under our experimental conditions, electrocoagulation was effective at low coagulant doses (< 5 mg/L), whereas relatively higher coagulant doses (> 5 mg/L) facilitated electroflotation. The steps involved along with a simple schematic of electroflotation and electrocoagulation as practiced in this research are detailed in the Appendix. Total aluminum concentrations generated during electrolysis were measured by atomic absorption spectroscopy (Flame AA-AAnalyst 300) after acidification with 36 N HCI.

Constant pressure, unstirred dead-end microfiltration was performed using PVDF membranes with 0.22-µm pores and 4.1 cm² effective area (GVWP02500 Durapore and Model 8010, Millipore). The filter cake was weighed after drying the membrane to a constant weight for 24 h at 35 °C. LabView (version 8.5) data acquisition software was used to collect instantaneous operating parameters at a variable rate (0.05 – 1.0 Hz) over the course of filtration using the following instrumentation: pressure (PX303-050G5V, Omega), temperature (TJ120 CPSS 116G, Omega), pH (Orion 9202BN, Thermo Orion), and cumulative mass of permeate (Ohaus Navigator N1H110, Fisher Scientific). The cumulative permeate volume was exponentially smoothed using a damping factor of 0.3 prior to numerical differentiation to calculate the instantaneous flux. All experiments were carried out at pH 6.4, which is effective for Al electrocoagulation pretreatment to MF (Ben Sasson and Adin 2010a, Gamage and Chellam

2011b) and optimal for electroflotation by generating a large number of smaller-sized hydrogen bubbles (Sarkar et al. 2010).

3.2.3. Particle imaging

Past research has shown that flocs formed during electrochemical pretreatment tend to break during measurements using an electrical sensing zone device (Multisizer III, BeckmanCoulter) (Gamage and Chellam 2011b). To this end, flocs were observed under an optical microscope (Olympus BX51, USA) to quantify their size and fractal dimension. Electrocoagulated/electrofloated water samples (0.1 mL) were placed on glass slides using a pipette with its tip cut to 5-mm diameter and excess water was carefully removed with tissue paper. Phase contrast images were obtained using a 10x objective (UPLFLN PH 10x / 0.3) at a working distance of 10 mm.

The electrocoagulated and electrofloated flocs were photographed using a high resolution digital camera (DP72, Olympus, Japan) mounted on a microscope to obtain RGB images with 1360 x 1024 pixel resolution. The microscope was calibrated using a graduated microscale and images were analyzed with cellSens Dimension (v 1.3, Olympus, Japan) software to obtain floc sizes. The flotsam obtained in electroflotation and well-mixed samples in electrocoagulation were diluted with nanopure water to image individual flocs. Lower particle concentrations in the water column following electroflotation did not necessitate any dilution for the MF feed water in this case. The projected area of the flocs was determined as the difference between the total floc area and the total area of voids and the characteristic length was the diameter of the smallest circle completely encircling a single aggregate.

2D fractal dimensions $d_{f,2D}$ were obtained by digitally analyzing the images (ImageJ Version 1.45S) with the box counting technique (Bushell et al. 2002),

$$d_{f,2D} = \lim_{L \to 0} -\frac{\log(N)}{\log(L)}, \qquad (4)$$

where N is the minimum number of square boxes required to completely cover the aggregate and L is the box size. The fractal dimension was obtained as the slope of the log-log plot of the number of squares against the corresponding resolutions of the square boxes.

3.2.4. Static light scattering

Mass fractal dimensions of the electrocoagulated and electrofloated aggregates ($d_{f,30}$) were measured using static light scattering (SLS, BI-200SM Brookhaven Instruments) equipped with a He-Ne laser (wavelength, $\lambda = 632.8$ nm) and a BI-9000AT correlator. Scattered intensities were recorded at angles θ between 14° and 75°, which was determined to be the linear fractal range during preliminary experimentation. The disturbance from dust was minimized by using the built-in statistical dust rejection function and setting a light rejection ratio of 3.0. To reduce multiple scattering, sedimentation, and excessive count rates, flocs were broken (assuming self-similarity at all length scales) by applying high shear and diluted in 25% glycerol (1 mL sample + 19 mL 25% glycerol) prior to analysis to increase the viscosity (i.e., delay floc sedimentation). The scattered intensity (I) was corrected for the refractive index (n) and background scattering. Data were collected as a function of the scattering vector, q = $(4\pi n/\lambda)\sin\theta/2$, to probe length scales (q⁻¹) between 39 to 290 nm. Background correction was made by measuring intensities arising from the 25% glycerol liquid medium used for dilution immediately before each analysis.

The fractal dimension of aggregates was calculated using Rayleigh-Gans-Debye theory (RGD, $I \alpha q^{-d_{f,3D}}$) (Harif and Adin 2011, Jarvis et al. 2005), which is applicable when $R_a^{-1} \ll q \ll R_p^{-1}$ for dilute suspensions of uniform primary particles with low refractive index (where R_a and R_p are the radii of the aggregate and the primary particle, respectively). The

exponent in the RGD theory does not strictly correspond to the fractal dimension (Bushell et al. 2002) when applied to aggregates formed from polydisperse natural colloidal suspensions typical of surface waters (Amal et al. 1990, Guan et al. 1998, Harif and Adin 2011); however, the scattering exponents are representative of fractal dimensions (Harif and Adin 2011) and those reported herein are an average of at least three separate SLS measurements from each sample.

3.2.5. Surface charge

The zeta potential was measured using a Nicomp ZLS instrument (Particle Sizing Systems, Santa Barbara, CA) at a fixed scattering angle of 14.7°. A He-Ne laser of wavelength 632.8 nm was used with a field strength of 4 V/cm and electrode spacing of 0.4 cm. The instrument was calibrated using a colloidal silica suspension standard of known zeta potential (Snowtex 50, Nissan Chemicals, Houston, TX). The electrophoretic mobility was converted to zeta potential using the Smoluchowski equation and each sample was run in three replicates of 30 seconds duration each.

3.2.6. X-ray photoelectron spectroscopy

Measurements of the fouled and clean membranes were performed using a PHI 5700 Xray photoelectron spectrometer (XPS) equipped with a monochromatic Al K α X-ray source (hv = 1,486.7 eV) incident at 90° relative to the axis of a hemispherical energy analyzer. Since the samples were insulating, analysis was done by turning on the neutralizer. Survey spectra in the range 0 – 1,400 eV were recorded for 5 minutes at 187.85 eV band pass energy on a spot diameter of 1.1 mm. High-resolution spectra were obtained for photoelectrons emitted from C 1s and Al 2p and O 1s at a 45° take-off angle. All spectra were collected at room temperature with a base pressure of 1 x 10⁻⁸ torr. Electron binding energies were calibrated with respect to the C1s line at 284.8 eV. PHI Multipak software (v. 5.0A) was used for data acquisition and analysis. The high-resolution data was first analyzed by background subtraction using the Shirley routine and nonlinear fitting to mixed Gaussian-Lorentzian functions. Atomic compositions were derived from the survey spectra. Peak areas were obtained after subtraction of the integrated baseline and corrected for sensitivity factors. More than three analyses at different regions on each membrane were performed to account for potential nonhomogeneities. Results were interpreted using the National Institute of Standards and Technology X-ray Photoelectron Spectroscopy Database (NIST Standard Reference Database 20, Version 3.5).

3.3. Results and Discussion

Approximately 25% of the experiments at different coagulant dosages and pressures were repeated. Paired t-tests conducted on instantaneous relative flux values and pH values from duplicate experiments showed no statistical differences at the 95% confidence level (Appendix Figure A7.4). The high consistency and reproducibility of our results allow comparison of experiments performed over the 9 month period of this study.

3.3.1. Physicochemical characterization of raw and pretreated MF feed waters

3.3.1.1. Elemental composition

The composition of colloids in the MF feed waters obtained through XPS survey scans and high resolution core line spectra are summarized in Table 3.1. As expected, AI and O dominated in electrochemically "treated" nanopure water due to Al(OH)₃ precipitation with adventitious carbon contributing c.a.13% to the elemental composition.

The elements C, N, and O in untreated raw water are attributed predominantly to NOM and microorganisms (Badireddy et al. 2008, Tipping 1981). As expected, the contribution of Al was low, which was verified by the City of Houston. Approximately 4% of Si was detected, a portion of which was assigned to crystalline SiO₂ (since a sharp peak was detected at 2 Θ = 26.6° in the X-ray diffractogram) potentially from quartz and diatoms (see Figure 3.8a). Crystalline

silica, in addition to amorphous silica, is often detected in natural waters (Cao et al. 2011, Tesson et al. 2009). Low amounts of Ca probably arise from CaSO₄/CaCO₃ in the shells of microfauna. Trace signatures of Na, Mg, P, S, etc. were also observed typical of surface water but not shown in Table 3.1.

O/AI C/AI C/N Sample C 1s Ca 2p Si 2p N 1s **O** 1s Al 2p ratio ratio ratio Nanopure water 66.7 19.6 0.67 13.1 --3.4 --(10 mg/L Al)4.9 0.83 3.6 10.57 Raw water (no Al) 51.8 37.1 0.42 44.7 62.4 Electrocoagulation 33.3 3.2 50.6 8.8 0.38 2.77 5.9 3.8 10.40 (10 mg/L Al)Electroflotation 27.4 1.6 0.30 0.4 2.2 57.8 12.4 4.7 17.13 (10 mg/L Al)

 Table 3.1. Percentage atomic concentrations of elements in untreated raw water and electrochemically treated suspensions.

Coagulant precipitation in pretreated natural waters increased the Al signal in electrocoagulated and electrofloated aggregates. In these waters, strong C, N, and O signals are again assigned predominantly to NOM and microorganisms (with some degree of adventitious carbon). As can be expected, the C/N ratio was conserved during electrocoagulation (10.4 versus 10.6 for untreated raw water) since the absence of a sedimentation step did not cause NOM removal. In contrast, floc flotation removed a portion of NOM and decreased both C and N; however, there was a net increase in the C/N ratio to 17.1 due to a greater decrease in the N signal compared with C (attributed to adventitious carbon).

Potential chemical functionalities were investigated in more detail using background subtracted high-resolution O 1s, C 1s, and Al 2p spectra of pretreated samples and curve fitted using Gaussian/Lorentzian functions (Figure 3.1). High relative concentrations of Al and O in solids formed in nanopure water corresponding to an O/Al ratio \rightarrow 3 (Table 3.1) indicates the presence of Al(OH)₃, which was confirmed by high resolution analysis of Al 2p and O 1s spectra.

First, the Al 2p peak was located at 74.55 eV, the value reported for Al in pure Al(OH)₃ (Crist 2005). Secondly, the –OH component of the O 1s peak at 532.2 eV comprised 89% of O (the remaining 11% corresponding to adventitious water at 533.6 eV). This contributed 3-times the Al amount in Table 3.1 resulting in a stoichiometric Al:OH ratio of 1:3, thereby proving the dominance of Al(OH)₃ rather than oxides or oxy-hydroxides (Crist 2005, Kloprogge et al. 2006). Further, X-ray diffraction analysis confirmed the amorphous nature of these precipitates as reported earlier (Gamage and Chellam 2011b, Masion et al. 1994).



Figure 3.1. High resolution XPS spectra of flocs formed during electroflotation: (a) oxygen in precipitates formed in nanopure water; (b) carbon in untreated raw water; (c) oxygen in pretreated raw water flocs; and (d) carbon in pretreated raw water flocs.

Natural organic and inorganic sources of oxygen increased the O/Al ratio in aggregates formed during electrocoagulation and electroflotation of surface water (5.9 and 4.7 respectively). These values are markedly higher than Al(OH)₃ formed in nanopure water (O/Al =

3.4). The O 1s peak (Figure 3.1c) was decomposed into: (i) a peak at 531.08 eV primarily due to bulk hydroxyl groups from Al(OH)₃ but also possibly from O-(C, H), including hydroxide, acetal, and hemiacetal; (ii) contributions from inorganic oxides such as Al₂O₃ and SiO₂ as well as carbonyl moieties (O = C in NOM) as in carboxylate, ester, or amide at 532.32 eV; and (iii) adventitious water and/or esters at 533.78 eV. These indicate the presence of carbohydrates, humic and fulvic acids, proteins and other components present in NOM (Tipping 1981). The high O/Al ratio in untreated raw water (\approx 45) is due to predominance of O from NOM and the very low Al concentration (only 0.12 mg/L measured through inductively coupled plasma mass spectrometry).

The C 1s core level peak in electrochemically treated waters was resolved to four components (Figure 3.1d): (i) aromatic and aliphatic C–C or C–H at 284.57 eV; (ii) a peak at 285.94 eV attributed to alcohols, ethers, or amines; (iii) carbonyl or amide groups at 288.05 eV; and (iv) carboxylates, carboxyl acids, or carbamates at 289.62 eV. The ~ 0.5 eV peak shifts for treated waters compared with raw water reveals changes to the electronic environment of C in the presence of Al(OH)₃ indicating NOM sorption on flocs (Guan et al. 2007).

In summary, XPS revealed (i) amorphous Al(OH)₃ and NOM as the major MF foulants in feed waters after both electrocoagulation and electroflotation pretreatment, (ii) electroflotation removed a fraction of the NOM by sorption/enmeshment onto Al(OH)₃, and (iii) no evidence of NOM oxidation during electrolysis since the relative intensities of the C 1s peaks at 285.94, 288.05, and 289.62 eV (corresponding to O=C and O-C) remained constant.

3.3.1.2. Colloid destabilization

The magnitude of the ζ potential decreased (i.e., less negative charge) with Al dose up to an intermediate value (20 mg/L in Figure 3.2), but maintained relatively constant positive charge at higher dosages (Gamage and Chellam 2011b, Holt et al. 2002). As reported earlier for conventional chemical coagulation (Wiesner et al. 1989b), charge neutralization of colloids occurs at an optimum dose corresponding to lowest fouling due to the adsorption of Al(OH)₂⁺ (the dominant hydrolysis species at pH 6.4). Note that this is unlike our recent result for electrocoagulation of Lake Houston water (Gamage and Chellam 2011a) where we reported sweep flocculation as the dominant destabilization mechanism. Hence, surface properties or concentrations of natural colloids appear to have changed over time in the source water. This points the need for frequent empirical evaluation of the optimal electrocoagulant dose, similar to jar testing for conventional chemical coagulation. Figure 3.2 illustrates that over the range of electrocoagulant dosages studied, particles were destabilized through a combination of double layer compression, charge neutralization, and sweep flocculation (see §3.3.1).



Figure 3.2. Floc surface charge was near neutral at optimum electrocoagulant dose.

3.3.1.3. Particle size

Optical images of raw water colloids and flocs formed in electrocoagulation and electroflotation (Appendix Figure A7.13) were used to calculate the area-weighted effective diameter. As summarized in Figure 3.3, the mean particle size in electrofloated MF-feed

suspensions increased up to an intermediate AI dosage (10 mg/L) and remained relatively constant for AI \ge 10 mg/L. In contrast, floc sizes increased monotonically with electrocoagulant dose. Also, MF feed waters following electrocoagulation and electroflotation pretreatment were similar in size and mass concentration for low doses (\le 5 mg/L) before significant bubble formation.

Greater AI dosages corresponding to longer electrolysis durations facilitated floc flotation, which reduced the size (and mass concentration) of colloids in the MF feed water pretreated with electroflotation compared with electrocoagulation. Note that smaller colloids also experience a lower collision frequency with hydrogen bubbles. Hence, under our experimental conditions the saturation hydrogen concentration was exceeded, a sufficient number hydrogen bubbles necessary for floatation were released from the cathode, and the threshold aggregate size for an adequate number of collisions was obtained for dosages greater than ~ 5 mg Al/L.



Figure 3.3. Area weighted mean particle diameters of electrocoagulated and electrofloated flocs measured with light microscopy.

3.3.1.4. Fractal dimensions/Scattering exponents

Three trends can be observed in Figure 3.4, which summarizes the scattering exponents (fractal dimensions) of the pretreated colloids in MF feed waters. First, as expected the 3D fractal dimensions measured by static light scattering were always higher than the corresponding 2D values measured by box counting. Secondly, fractal dimensions of electrocoagulated and electrofloated flocs were almost identical (both d_{f,2D} and d_{f,3D}) revealing that the structure of the colloidal foulants reaching the membrane surface was similar for any given set of pretreatment conditions. Finally, more loosely-packed aggregates were formed evidenced by decreasing $d_{f,2D}$ and $d_{f,3D}$ (Lee et al. 2003) with increasing Al dose up to ~ 15 mg/L after which fractal dimensions remained relatively constant. Reductions in the fractal dimension with increasing addition of AI (0 - 15 mg/L) is attributed to progressive neutralization of colloidal surface charge (as explained in §3.3.1.2. and Figure 3.2) and increasing attachment efficiency. Higher Al dosages (≥ 15 mg/L) did not significantly influence aggregate morphology because sweep flocculation dominated and the ζ potentials remained constant. Mass fractal dimensions $(d_{f,3D})$ changed from 2.6 to 2.0, which agrees with values reported for polydispersed suspensions (Amal et al. 1990, Vahedi and Gorczyca 2010). The values at the upper end of this range correspond to particle-particle and particle-cluster interactions with a high energy barrier before effective charge neutralization. Cluster-cluster interactions dominated aggregation for higher dosages during sweep flocculation (Amal et al. 1990).

In summary, the surface charge and structure of colloidal aggregates in electrocoagulated and electrofloated waters were similar. The removal of larger floating aggregates during electroflotation pretreatment resulted in smaller colloids in MF feed waters and decreased mass loading to the microfilter. The O/Al ratio of 4.7 in electroflotation was closer to the stoichiometric value of 3 in Al(OH)₃ compared with electrocoagulation (5.9),

suggesting the relative dominance of $Al(OH)_3$ colloids following electroflotation pretreatment. Moreover, the C/Al ratio was lower in electroflotation indicating that flocs in the effluent of this pretreatment process were enriched in Al relative to NOM. These physicochemical differences in the microfilter feed water following electrocoagulation and electroflotation can be expected to cause dissimilar fouling which is reported next.



Figure 3.4. 2D and 3D fractal dimensions decrease with increasing electrocoagulant dosage.

3.3.2. Improvements in microfilter flux following electroflotation pretreatment

As summarized in Figure 3.5a, the untreated surface water severely fouled the microfilter causing more than 90% reduction in flux within 100 L/m² (i.e., 20 minutes). Electroflotation pretreatment significantly improved fluxes with increased AI dosage up to 10 mg/L. Interestingly, increasing AI dosage beyond the optimal value reduced the flux and yielded similar profiles for all higher AI concentrations evaluated (15, 20, and 30 mg/L). Flux improvements with increasing AI dose up to the optimal value is due to the combined effects of (i) increasing particle size (§3.3.1.3, Figure 3.3), (ii) formation of more permeable aggregates (§3.3.1.4, Figure 3.4), and (iii) reduced cake mass (discussed later in §3.3.3 and lower left inset in

Figure 3.6). Overlapping flux profiles for Al \geq 15 mg/L is attributed to very similar feed water characteristics, including aggregate size, fractal dimension, and cake mass. Raw water fouling profiles exhibited an initial intermediate blocking period followed by cake filtration as revealed by empirical fits to constant pressure blocking laws (Bagga et al. 2008b, Hermia 1982b, Xu and Chellam 2005). In contrast, the entire fouling profiles for pretreated waters were quantitatively modeled solely by cake filtration potentially due to the higher mass loading and larger sizes of feed water colloids (Bagga et al. 2008b). Figure 3.5b shows that fouling was exacerbated by increasing the transmembrane pressure for pretreatment at the optimal dosage due to compaction of aggregated natural colloidal materials comprising the cake (Bagga et al. 2008b, Gamage and Chellam 2011b).



Figure 3.5. (a) Improvements in relative permeate flux only up to an intermediate value of aluminum dosage (10 mg/L) at a constant transmembrane pressure of 13.8 kPa following electroflotation pretreatment. (b) Fouling worsens with increasing pressure during electroflotation-microfiltration.

3.3.3. Comparison of electroflotation and electrocoagulation pretreatment

3.3.3.1. Effects of operating conditions on flux profiles

Representative flux profiles comparing electrocoagulation and electroflotation are summarized in Figure 3.6. Under our experimental conditions, the two pretreatment techniques both worked optimally at the same Al dosage (10 mg/L) in terms of MF fouling control. Both pretreatment methods resulted in nearly identical permeate fluxes below the optimal Al dosage (e.g., Figure 3.6a). This is a direct consequence of their similar effluent water characteristics reported in §3.1 before significant bubble formation during electrolysis. Importantly, electroflotation pretreatment resulted in higher fluxes at or beyond the optimal Al dosage once the threshold number of bubbles was released (Figure 3.6b, c, and d). The properties of the membrane cake layer were analyzed in more detail to mechanistically understand why electroflotation outperformed electrocoagulation.



Figure 3.6. Comparison of instantaneous normalized fluxes following electrocoagulation and electroflotation pretreatment at different operating conditions: (a) 13.8 kPa, 5 mg Al/L; (b) 13.8 kPa, 10 mg Al/L; (c) 163.6 kPa, 10 mg Al/L; and (d) 13.8 kPa, 20 mg Al/L.

3.3.3.2. Cake resistances and compression

Increasing transmembrane pressure caused greater fouling as observed in the corresponding profiles in Figure 3.6b and c and Figure 3.5b due to cake compaction (Bagga et

al. 2008b, Gamage and Chellam 2011b, Tiller et al. 1987b). The compressibility index increased from raw water (0.48), to electroflotation pretreatment (0.59), and to electrocoagulated colloids (0.74). This suggests a higher extent of aggregate breakage and the rearrangement of primary particles for electrocoagulation pretreatment presumably due to the higher floc size.

Similar fouling profiles for less than optimal AI dosages (0, 2, and 5 mg/L in Figure 3.6a) translated to statistically similar total and specific cake resistances for both pretreatment processes (Figure 3.7). Under these conditions, bubble formation was insignificant and associated particle removal by flotation was negligible. This resulted in nearly identical cumulative cake masses (three overlapping data points in the lower right inset in Figure 3.7). Hence, the corresponding specific cake resistances were also indistinguishable between electrocoagulation and electroflotation (upper left inset in Figure 3.7). Higher fluxes measured for electroflotation pretreatment at Al \geq 10 mg/L (e.g., Figure 3.6b, c, and d) implied lower cumulative cake resistances for this pretreatment method. Longer electrolysis durations facilitated particle removal by flotation and hydrogen bubble evolution significantly reduced total mass loading onto the microfilter. As seen in the lower right inset of Figure 3.7, the cake mass increased monotonically with dose for electrocoagulation whereas it reached a relatively constant and lower value for electroflotation beyond the optimal dosage. Even though electroflotation with Al \geq 10 mg/L reduced cake mass, it increased the specific resistance compared with electrocoagulation since it produced smaller particles (Figure 3.3). Conversely, formation of larger particles and associated lower specific resistances by electrocoagulation was counteracted by the disproportionately higher mass of colloidal matter filtered by the membrane (i.e., higher cumulative resistance).

Scanning electron micrographs of membranes fouled with raw water (Figure 3.8a) revealed that natural colloidal matter was highly heterogeneous. Diatoms were observed,
which contributed to the Si signal obtained in both XRD and XPS measurements (§3.3.1). Electrocoagulation pretreatment produced a thick cake layer of amorphous $Al(OH)_3$ flocs, which appeared to have enveloped the particles present in raw water (Figure 3.8b). In contrast, a very thin cake layer was visualized for electroflotation pretreatment, which also easily peeled off following dehydration that was necessary for electron microscopy (Figure 3.8c).



Figure 3.7. Comparison of electrocoagulation and electroflotation in terms of total cake resistance, specific cake resistance, and cake mass.

3.3.3.3. Evidence of a slightly higher degree of irreversible fouling after electrocoagulation

pretreatment.

XPS was performed on clean membranes and on membranes that were used to filter waters pretreated by electrocoagulation and electroflotation. Note that XPS was conducted on the fouled membranes only after removing the cake which easily peeled off following overnight drying at a low temperature of 35 °C (Table 3.2).

Sample	C 1s	N 1s	O 1s	F 1s	Al 2p	Si 2p	O/Al ratio	C/Al ratio
Clean membrane	57.7	-	13.5	28.8	-	-	-	-
EC membrane	50.7	1.6	22.5	21.2	3.4	0.61	6.2	14.9
EF membrane	48.7	-	18.9	29.2	3.1	-	6.1	15.7

 Table 3.2. Relative percentage elemental concentrations detected in clean membranes and fouled membranes after removing the cake layer.

In all cases, the major components were C, O and F where F and a majority of C were attributed to the PVDF polymer constituting the filters. The increasing oxygen fraction in fouled membranes after both types of pretreatment was attributed to Al(OH)₃ and NOM. The appearance of N and Si only in membranes that filtered electrocoagulated water suggests that NOM and silica contributed to irreversible fouling. Notably, the absence of N and Si in membranes after electroflotation indicates that this pretreatment technique effectively reduced irreversible organic and silica fouling. As revealed in Figure 3.8c, the exposed membrane (after the cake easily peeled off after low-temperature sample dehydration) resembled the clean membrane, which suggests largely reversible binding between the colloids and the membrane after electroflotation. A greater degree of irreversible fouling after electrocoagulation is attributed to the higher NOM concentrations. Since electroflotation removed a fraction of the NOM present in the raw water (due to the intermediate particle removal/flotation step) the cake was bound less strongly to the membrane, thus facilitating its removal. Even though more Al(OH)₃ relative to NOM was transferred to MF in electroflotation (§3.3.1.1), Table 3.2 reveals that the O/AI ratio and the amount of AI present on the membrane were conserved in both pretreatment processes. The remaining AI is attributed to colloidal $AI(OH)_3$ irreversibly bound to the fouled membranes after filtration of pretreated waters.



Figure 3.8. Scanning electron micrographs of fouled membranes: (a) after filtering 150 mL of untreated Lake Houston water, (b) after filtering 150 mL of 10 mg/L electrocoagulated water, and (c) after filtering 150 mL of 10 mg/L electrofloated water.

3.4. Conclusions

Substantial floc flotation occurred when electrolysis was performed for sufficiently long durations (i.e., high Al dosages). A significant advantage of electroflotation is intermediate floc removal (without adding a separate step in the treatment train), which reduces the concentration of colloids in the water column to be removed by microfiltration. Microfiltration of pretreated waters with lower concentrations of colloids and NOM following electroflotation improved fluxes to a greater extent than electrocoagulation. Unlike chemical and electrocoagulation pretreatment, MF fluxes did not continue to decline progressively with AI overdosing in this process. This suggests the possibility of easier process control with electroflotation-MF. Additionally, the range of minimum Al solubility (~ pH 6.4) coincides with the pH range for release of a large number of smaller hydrogen bubbles, which aids in flotation by increasing attachment frequency. Further, colloids in MF feed waters after electroflotation were largely reversibly bound to membrane surfaces whereas some irreversible fouling was measured in electrocoagulation. This suggests comparatively greater MF backwashing efficiencies for electroflotation pretreatment. These characteristics make electroflotation highly suitable for low-pressure membrane pretreatment during municipal drinking water purification. It should be emphasized that more work is necessary to scale-up these relatively short-term bench-scale observations to pilot- and full-scale before recommendations can be made for realworld systems.

Chapter Four. Mechanisms of Physically Irreversible Fouling during Surface Water Microfiltration and Mitigation by Aluminum

Electroflotation Pretreatment

4.1. Introduction

Microfiltration (MF) and ultrafiltration (UF) membranes are highly effective in removing protozoa, bacteria, colloidal matter, and turbidity from contaminated waters. However, deposition of filtered constituents on the surface or within the pores decreases membrane productivity, which is an important deterrent to their increased implementation. Short-term MF/UF fouling is almost universally combated by hydraulic regeneration; e.g., backwashing every 10-30 min or so, which however does not fully restore the initial membrane permeability (Chellam et al. 1998b).

Since physical regeneration methods such as backwashing are only partially effective in controlling fouling, colloids and natural organic matter (NOM) present in the source water are sometimes also coagulated prior to MF/UF to better maintain productivity (Huang et al. 2009, Lahoussine-Turcaud et al. 1990b). Past research has largely focused on optimizing conventional coagulation conditions to best control short-term fouling during forward filtration (Choi and Dempsey 2004b, Judd and Hillis 2001, Schäfer et al. 2001, Wiesner et al. 1989a) over and above what is possible by backwashing alone, by reducing pore penetration and increasing cake permeability. Recently, there is developing interest in an alternative to chemical coagulation (i.e., external addition of aluminum/ferric salts), wherein the coagulant is generated *in situ* through electrolytic oxidation of a sacrificial Al/Fe anode (i.e., electrocoagulation) (Cañizares et al. 2006a, Tanneru et al. 2013, Zhao et al. 2010b). Simultaneously, cathodic reduction of water evolves hydrogen gas inducing floc-flotation (i.e., electroflotation) (Chen et al. 2002b). Since

electroflotation pretreatment removes a portion of NOM and silica and significantly improves short-term MF flux (Gamage et al. 2012), we hypothesize that it will also successfully combat irreversible fouling over extended timeframes. In general, adsorption of NOM (Gu et al. 1994, Howe and Clark 2002b, Kim and Dempsey 2008, Lahoussine-Turcaud et al. 1990b, Laine et al. 1989) or its specific components including protein-like, carbohydrate-like, and humic substances (Peldszus et al. 2011, Yamamura et al. 2007b) as well as inorganic constituents such as silicon, iron, and aluminum (Howe and Clark 2002b, Yamamura et al. 2007a, Yamamura et al. 2007b) are typically linked to operationally observed fouling. More detailed information on the dynamics of foulant accumulation will aid in understanding MF flux decline mechanisms.

The objective of this research is to rigorously elucidate changes in foulant chemical composition during progressive physically irreversible fouling of a commercially available modified poly(vinylidene fluoride) (PVDF) membrane during MF of untreated and pretreated Lake Houston water. Operational improvements in flux over five filtration/regeneration cycles (i.e., reductions in reversible and irreversible fouling) achieved by electroflotation pretreatment were evaluated. Foulants present in the raw water and the mechanisms by which they were removed during electroflotation pretreatment were identified using Attenuated Total Reflectance – FTIR spectroscopy (ATR-FTIR) and X-ray Photoelectron Spectroscopy (XPS). In addition to chemical fingerprinting, foulant complexation on membrane surfaces was probed through intensity changes in C(=O)O⁻ stretching vibrations region of IR spectra.

4.2. Materials and Methods

4.2.1. Source water quality

Important physicochemical properties of the Lake Houston water sample were: pH 7.60 \pm 0.19, turbidity 14.7 \pm 1.5 NTU, alkalinity 71 \pm 2 mg/L as CaCO₃, calcium hardness 48 \pm 3 mg/L as CaCO₃, conductivity 328 \pm 13 μ S/cm, dissolved organic carbon (DOC) 4.9 \pm 0.5 mg/L, and UV₂₅₄

0.143±0.005 cm⁻¹. The ζ potential of natural colloids was -17±2 mV. The iron concentration (0.07±0.03 mg/L) was very low compared with aluminum (0.21±0.04 mg/L) and silicon (2.5±0.3 mg/L). Proteins and carbohydrates were measured as 0.24 mg/L and 0.75 mg/L respectively by colorimetry (Badireddy et al. 2010). The pH was reduced to 6.4 using 0.1N HCl before microfiltering untreated raw water.

4.2.2. Microfiltration

Bench-scale, unstirred, dead-end MF was performed at a constant pressure of 14 kPa using modified PVDF disc filters (0.22 μm, 4.1 cm², GVWP02500 Durapore, Millipore). This membrane was chosen to simulate many commercially successful MF/UF membranes used in large-scale environmental applications such as GE-Zenon Zeeweed, Pall-Asahi Microza LGV, Siemens-Memcor, and Dow-Omexell, all of which are based on PVDF chemistry. First, 100 mL of nanopure water was passed through the virgin membrane to calculate its permeability. Next, 100 mL of feed suspension (untreated or electrofloated water) was filtered. During this time, the transmembrane pressure (PX303-050G5V, Omega) and cumulative permeate volume (Ohaus Navigator N1H110, Fisher Scientific) were monitored digitally at a variable rate (0.05-1 Hz) to quantify instantaneous fouling rates (Gamage et al. 2012).

Fouled membranes were physically regenerated using a 3-step procedure. In the first step, the membrane was carefully removed from the cell and its surface was rinsed with a jet of nanopure water to dislodge the loosely adhered cake layer (simulating fast flushing). Separately the filtration cell was also rinsed with nanopure water. Secondly, similar to earlier work (Kimura et al. 2004, Kimura et al. 2008, Yamamura et al. 2007a), the remaining thin gel-like layer was gently wiped with a fine tissue and the membrane was replaced upside-down in the cell. Thirdly, 100 mL nanopure water passed through the upside-down membrane (representing backwashing) at 17 kPa. The entire filtration and regeneration procedure constitutes one cycle

and was repeated five times for untreated and electrofloated water. Finally, the membrane orientation was reversed to the original direction and clean water flux again recorded to quantify the progressive buildup of irreversible fouling. Control experiments using nanopure water revealed that this regeneration procedure did not affect the virgin membrane permeability over 5-cycles. After cycles 1 and 5, membranes were immersed in 25 mL of HCl (pH 2) and kept in a reciprocating shaker (220 rpm) for 200 minutes at 40 °C. This process was repeated using NaOH (pH 12). DOC and Al removed from the membranes were measured to estimate the mass of NOM and Al accumulated during fouling.

4.2.3. Electrochemical pretreatment

Galvanostatic electrolysis was performed at an initial pH of 6.4 and 20 mA/cm² current density to achieve a dosage of 10 mg/L as Al, corresponding to optimum conditions for shortterm forward filtration fouling control (Gamage and Chellam 2011b, Gamage et al. 2012). The pH increase during electrocoagulation was small, remaining within 0.2 units. Colloids were efficiently destabilized at this dosage (ζ potential \rightarrow 0; averaging 0.05 mV). The cylindrical Perspex cell consisted of an Al anode (Puratronic, 99.9965% as Al, Alfa Aesar) with an active surface area of 12.3 cm² and a porous annular 316-stainless steel cathode. After electrolysis, the cell contents were drawn out from the bottom leaving behind the floated flocs at the top of the water surface and reducing mass loading onto the membrane. Faradaic dissolution of trivalent aluminum ions at near 100% efficiency was observed under these conditions and confirmed by atomic absorption spectroscopy (Flame AA-AAnalyst 200). The predominant precipitate under these conditions is Al(OH)_{3(am)} (Gamage et al. 2012).

4.2.4. ATR-FTIR

Spectra were collected using a Nicolet iS10 FTIR spectrometer ATR accessory with a Ge reflection element (45° incidence angle), equipped with a mid-infrared Ever-Glo source, KBr/Ge

beam splitter, and fast recovery DTGS detector. Each reported spectrum is an average of 5 spectra, each consisting of 512 coadded scans at 2 cm⁻¹ resolution, 16 cm⁻¹ phase resolution, 20 kHz low-pass filter, a zero-filling factor of 2 using a Blackman Harris 4-step apodization, and Mertz phase correction. Spectra were obtained for (1) source water, (2) "pure" electrocoagulant precipitates generated in nanopure water (control experiment), (3 and 4) flocs floated to the surface and those suspended in the water column after electrochemical pretreatment of Lake Houston water, (5) wetted virgin membrane, and (6 and 7) irreversibly fouled membranes after cycles 1 and 5. Solids were vacuum-dried for 1h and the moist paste was pressed uniformly on the Ge crystal with maximum contact whereas membranes were analyzed as is. Spectral processing including baseline correction and subtraction was performed using OMNIC (v8.3) software. Second derivatives were employed to enhance resolution.

4.2.5. XPS

X-ray spectra were obtained using a PHI 5700 spectrometer equipped with a monochromatic Al K α X-ray source (hv = 1,486.7 eV) incident at 90° relative to the axis of a hemispherical energy analyzer. Samples were vacuum dried for 48 h and pressed on indium substrates (99.9975% as In, 0.25 mm thick, Alfa Aesar) prior to analysis. Dehydrated membranes were analyzed as is. Sample charging was controlled by the neutralizer. Survey spectra in the range 0-1400 eV were recorded for 5min at 187.85 eV band pass energy on a spot diameter of 1.1 mm. High-resolution spectra were obtained for photoelectrons emitted from C1s, O1s, Al2p, and F1s at 23.5 eV pass energy and 45° take-off angle. Potential heterogeneities were accounted for by averaging 5-7 spectra from different regions of each sample.

4.3. **Results and Discussion**

0.4

0.2

0.0

0

cycle-1

b

200

4.3.1. Foulants accumulated with repeated filtration/regeneration cycling and



(ir)reversible fouling was reduced by electroflotation pretreatment

600 Volume filtered per unit membrane area (L/m²)

cycle-3

cycle-4

Pretreated

lake water

800

(electroflotated)

1000

1200

cycle-5

Figure 4.1. (a and b) Instantaneous flux profiles over 5 filtration and hydraulic regeneration cycles for raw (untreated) water and pretreated (electrofloated) Lake Houston water respectively. The dotted line denotes irreversible fouling. Initial flux $J_0 = 910\pm15$ Lm⁻ $^{2}hr^{-1}$.

cycle-2

4.3.1.1. Flux profiles

Instantaneous flux profiles over five filtration/regeneration cycles for MF of raw and electrofloated Lake Houston water are shown in Figure 4.1a and b respectively from which major two trends are discerned. First, electroflotation well-controlled flux decline during forward filtration; e.g., only 58% loss in productivity during the first cycle (J/J_o from 1 to 0.42 in Figure 4.1b) compared with 93% decrease (J/J_o from 1 to 0.07 in Figure 4.1a) for raw water. Since we have recently shown this to be due to the formation of larger flocs with low fractal dimension and relatively low colloidal mass loading to MF thereby decreasing pore penetration and cumulative and specific cake resistances (Gamage et al. 2012), it will not be discussed further herein. Secondly, productivity progressively declined with cycling suggesting increasing irreversible accumulation of foulants, which is the focus of this manuscript. The overall permeability after regeneration decreased more drastically for the untreated water where 80% of the virgin membrane flux was recovered after cycle-1 but only 47% after cycle-5. Importantly, electroflotation pretreatment enhanced physical regeneration recovering 93% of the virgin membrane flux after cycle-1 and 69% after cycle-5 (Figure 4.1b).

4.3.1.2. Foulant elemental concentrations

XPS survey scans did not detect any fluorine in the feed waters but a strong F signal was detected from all membranes indicating that the foulant layer after regeneration was thinner than the XPS sampling depth (~5 nm). Therefore, XPS profiled the entire foulant layer after physical regeneration in all cases. Moreover, atomic concentrations at different locations exhibited low variability showing relatively uniform foulant deposition throughout the membrane surface (Appendix Table A7.2). The attenuation of the F-signal upon foulant deposition was used to account for virgin membrane contributions to C- and O-atomic concentrations on fouled membrane surfaces (Appendix Table A7.1). Adjustments were not



necessary for N, Si, and Al as they were absent in the virgin membrane.

Figure 4.2. (a) Increasing aluminum, oxygen, carbon, nitrogen, and silicon atomic concentrations on the microfilter surface over multiple filtration and regeneration cycles for raw Lake Houston water. (b) Reduced atomic concentrations of C, N and Si and concomitant increase of Al and O on the membrane surface following electroflotation pretreatment compared with membranes fouled with raw water. C- and O-data were adjusted using the attenuation of the F-signal (Riviáere and Myhra 1998). (c) Atomic concentration ratios for MF feed waters (raw and after electroflotation) and "pure" coagulant formed by electrolyzing nanopure water.

C, O, N, Si, and Al progressively accumulated on the membrane surface with repeated

cycling for both untreated and pretreated feed waters as seen in Figure 4.2a and Figure 4.2b respectively. For raw water-MF, the dominant irreversible elemental foulants were O and C followed by Si, N, and Al (Figure 4.2a) whereas for pretreated waters O, Al, and C were dominant with Si and N only playing minor roles (Figure 4.2b). Also as seen in Figure 4.2a and Figure 4.2b, introducing pretreatment increased irreversible accumulation of Al and O but decreased C, N,

and Si concentrations on membrane surfaces compared with untreated raw water. The marked increase in Al and O atomic concentrations on regenerated membrane surfaces after pretreatment compared with the untreated water signifies accumulation of Al(OH)_{3(s)} generated during electroflotation pretreatment (O was approximately 3x higher than Al on pretreated membranes (Gamage et al. 2012)) similar to earlier reports with polyaluminum chloride coagulation (Kimura et al. 2008). This was confirmed by analyzing Al in chemical cleaning solutions, which showed >10x greater Al accumulation after cycle 5 (0.012 mg/cm²) following electroflotation pretreatment compared to untreated raw water (0.001 mg/cm²). Further, pretreatment shifted the particle size distribution of the raw water colloids towards greater sizes (Appendix Figure A7.18). Hence, significant improvements in flux after physical regeneration despite considerable accumulation of coagulant is attributed to reduced pore penetration following electroflotation pretreatment (Gamage et al. 2012).

Si and N atomic concentrations were below detection limits for "pure" coagulant generated in nanopure water but increased to 2.90% and 2.02% respectively in electrochemically treated natural water flocs (Figure 4.2c). Adventitious C contributed 9.68% to precipitates generated by electrolyzing nanopure water. C atomic concentration increased to 32.76% in flocs formed in Lake Houston water. These increases signify sorption of siliceous, nitrogenous, and carbonaceous foulants from the source water onto electrochemically generated flocs during pretreatment. Hence, the depletion of Si, N, and C from irreversibly fouled membranes filtering pretreated waters can be explained by their removal during electroflotation that reduced their feed water concentrations subsequently reducing fouling. Membrane surface DOC concentrations determined by analyzing chemical cleaning solutions were 0.011mg/cm² after cycle-1 and 0.068mg/cm² for untreated water after cycle-5. These reduced to 0.007mg/cm² and 0.038mg/cm² for membranes filtering electrofloated water after

cycles 1 and 5 respectively, confirming carbon removal during pretreatment. Therefore, irreversible fouling control by electroflotation pretreatment can be explained by reduced penetration of foulants into membrane pores and foulant removal by floc flotation before MF (in spite of coagulant accumulation on the membrane). Foulant sorption during electroflotation is discussed in more detail later in the section "Foulant removal from source water during electrochemical pretreatment."

4.3.1.3. Foulant functional groups

FTIR spectrum of the untreated source water is shown in Appendix Figure A7.19 and corresponding peak assignments in Appendix Table A7.6. As shown in Appendix Figure A7.19, amide I (1700-1600cm⁻¹) and amide II (1570-1545cm⁻¹) bands were weaker than those of carbohydrate-like and siliceous compounds (3750-3300 and 1200-900cm⁻¹). XPS also measured lower atomic concentration of N compared with Si (Figure 4.2e). Further, colorimetry revealed lower concentrations of proteins (0.53mg/L) than carbohydrates (1.17mg/L). Hence, protein-like substances were present in lower concentrations compared with carbohydrate-like and siliceous substances in Lake Houston water. Source water foulants are described in more detail in the SI.

IR spectra of membrane surfaces after cycles 1 and 5 are shown in Appendix Figure A7.20 for raw and electrofloated feed waters. Band intensities corresponding to carbohydrates (vO-H 3750-3300cm⁻¹, vC-O-C/vC-O 1200-900cm⁻¹, vC-O-C 820-750cm⁻¹), proteins/amino sugars (vN-H 3400-3050 cm⁻¹, vC=O/δNH₂ 1650 cm⁻¹, δN-H/vC-N 1540 cm⁻¹, vC-O-C 1036 cm⁻¹), humic acids (vC-H 3050-2800 cm⁻¹, vC=C-C 1510-1450 cm⁻¹, v(C=O)O⁻ 1700-1300 cm⁻¹, vC=O 1730 cm⁻¹), and silica (vSi-O-H 3750-3300 cm⁻¹, vSi-O-Si 1100 cm⁻¹, 800 cm⁻¹, and 780 cm⁻¹) increased from cycle-1 to cycle-5 for membranes irreversibly fouled by raw water. Therefore, as shown previously for a single cycle (Howe and Clark 2002b, Kim and Dempsey 2008, Laine et al. 1989, Lee et al. 2006), carbohydrate-like, proteinaceous, humic substances, and siliceous compounds

were major irreversible foulants over multiple filtration/regeneration cycles as well. Irreversible accumulation of organic foulants with number of cycles during raw water-MF was also confirmed by analyzing chemical cleaning solutions (6-fold increase from 0.011±0.005 mgDOC/cm² after cycle 1 to 0.068±0.01 mgDOC/cm² after cycle 5). For membranes subjected to electroflotation pretreatment, regions corresponding to O-H (3650-3200 cm⁻¹) and Al-O (850-680 cm⁻¹) stretching vibrations significantly intensified even after cycle-1 compared with the virgin membrane and membranes fouled by the raw water (Figure A7.20). The intensity further increased for cycle-5. Analysis of chemical cleaning solutions also showed irreversible Al accumulation with number of cycles (5-fold increase from 0.002±0.001 mg/cm² after cycle 1 to 0.010±0.002 mg/cm² after cycle 5). Hence, IR spectra, chemical cleaning, and XPS (Figure 1d) all demonstrate progressive Al(OH)_{3(s)} coagulant accumulation on membranes filtering pretreated water.

4.3.2. Irreversible fouling during direct MF of Lake Houston water (no pretreatment)

FTIR spectra of membranes filtering untreated and pretreated waters were analyzed in more detail to rigorously identify changes in foulant composition with successive filtration/regeneration. Only spectra corresponding to untreated water are discussed in this section but spectra following electroflotation are discussed in the next section.

4.3.2.1. Hydrophobic molecules contribute more to fouling during early stages of filtration

As seen in Figure 4.3, the O-H/N-H band at 3650-3300 cm⁻¹ was attenuated while C-H bands maintained their intensity even after cycle-1 (dotted blue line) compared with the virgin membrane (green line). Hence, fouling appears to have been initiated by irreversible binding of less polar (more hydrophobic) compounds since the OH/NH band is an indicator of hydrophilicity (Thurman 1985).



Figure 4.3. ATR-FTIR spectra of the virgin membrane (green line), irreversibly fouled membrane surfaces operating on electrofloated water (solid red cycle-5 and dotted red cycle-1) and untreated Lake Houston water (solid blue cycle-5 and dashed blue cycle-1) corresponding to CH, OH, and NH stretching vibrations. Source water spectrum (dashed black line) is also shown. Peaks corresponding to hydrogen bonding: vO-H/ vN-H 3800-2500 cm⁻¹, vC=O/δNH₂ 1680-1620 cm⁻¹, δN-H/vC-N 1550-1520 cm⁻¹; Peaks related to interactions of hydrophobic molecules: vC-H 3050-2800 cm⁻¹.

The spectrum of the wetted virgin membrane surface was subtracted from those of irreversibly fouled membranes to obtain the difference spectra shown in Figure 4.4. Amide I (1620-1680 cm⁻¹) and amide II (1520-1550 cm⁻¹) bands after cycle-1 were very weak in the membrane surface difference spectrum (dashed blue line in Figure 4.4). However, they significantly intensified over extended timeframes, achieving similar intensities after 5-cycles (solid blue line in Figure 4.4) to those measured in untreated Lake Houston water (dotted black line in Figure 4.4). More intense N-H vibrations (3400-3050 cm⁻¹) than O-H vibrations (3750-3300 cm⁻¹) signify substantial irreversible binding of protein-like substances with progressive

filtration/regeneration. In contrast, largely reversible binding of carbohydrate-like compounds to the membrane is inferred since they appear to have been effectively removed during regeneration evidenced by the substantially weaker bands (O-H 3750-3300 cm⁻¹ and C-O-C/C-O 1150-970 cm⁻¹) in the membrane difference spectrum compared with the raw water. This is potentially due to weaker interactions of these bulky molecules (Her et al. 2002) with the membrane due to steric hindrances. Hence, relative accumulation of protein-like substances on the membrane with respect to their feed water concentration appears to have been greater than carbohydrate-like substances. Therefore, as reported recently during UF of natural surface water (Peldszus et al. 2011) and model solutions of sodium alginate and bovine serum albumin (Wang et al. 2013), protein-like substances seem to have played an important role in irreversible fouling of MF membranes in spite of their lower feed water concentration. It is emphasized that since carbohydrates are typically more abundant in surface water they are expected to contribute more to fouling on an absolute basis (Yamamura et al. 2007b).



Figure 4.4. Difference spectra of irreversibly fouled membrane surfaces for electroflotation pretreatment (solid red line: cycle 5, dotted red line: cycle 1) and untreated raw water (solid blue line: cycle 5, dashed blue line: cycle 1). The raw feed water (dotted black line) spectrum is also shown. Peaks corresponding to complexation interactions: $v_{as}(C=O)O^{-}$ 1650-1500 cm⁻¹, $v_s(C=O)O^{-}$ 1500-1350 cm⁻¹, vC=O 1730 cm⁻¹.

4.3.2.2. Hydrophilic molecules and NOM complexation determine fouling after repeated filtration/regeneration

In contrast to cycle-1, the O-H/N-H band significantly intensified after cycle-5 even becoming more intense than C-H bands. Figure 1c also shows increasing O, N, and Si from cycle-1 to cycle-5 suggesting the accumulation of relatively more hydrophilic foulants and siliceous compounds as filtration progressed.

Since NOM-carboxyl groups in surface waters are partially protonated at environmental pH values (Collins et al. 1986, Thurman 1985), organic acids in Lake Houston are capable of both inner-sphere and outer-sphere complexation. As expected, the intensity of the 1800-1300 cm^{-1} $C(=O)O^{-1}$ stretching region substantially changed in the difference spectrum of fouled membranes after cycle-5 compared with that of the raw water (Figure 4.4). The carbonyl band at 1730 cm⁻¹ considerably attenuated whereas both symmetric (1425 cm⁻¹) and asymmetric $(1700-1500 \text{ cm}^{-1})$ stretching C(=O)O⁻ bands simultaneously intensified indicating deprotonation of carboxylic groups upon foulant-membrane interactions (Biber and Stumm 1994, Omoike and vanLoon 1999). Increasing $v_{as}C(=0)O^{-}$: $v_{s}C(=0)O^{-}$ intensity ratio in Figure 4.4 is symptomatic of ligand exchange interactions of carboxylic groups with metals in untreated water (Gao et al. 2009). Hence, polyvalent cations appear to have mediated bridging (Mouvenchery et al. 2012) and/or chelation (Nakamoto 2009) between NOM-COOH groups and the fouled membrane surface. Further evidence for bridging/chelation was provided by the separation distance between symmetric and asymmetric stretching bands (Gao et al. 2009, Nakamoto 2009) ($\Delta v =$ $v_{as}C(=0)O^{-} - v_{s}C(=0)O^{-}$ being in the range 75-230 cm⁻¹. Outer-sphere complexation should have also contributed to these observed peak changes since the overall surface charge of colloids was negative (Gao et al. 2009) (ζ potential=-17±2 mV).

Iron concentrations were very low in the source water and Fe2P and Ca2P signals were

absent on fouled membranes (Figure A7.21a). In contrast, aluminum was present in the source water and the Al2P signal was observed both in the raw water (Figure 4.2e) and on irreversibly fouled membranes (Figure A7.21b). Aluminum exhibits greater affinity to organic ligands than calcium (Sposito 1996) and its atomic concentrations on fouled membrane surfaces increased with cycling (Figure 4.2c and Figure A7.21b). Additionally, calcium was detected in the cake layer spectra (Gamage et al. 2012) (Figure A7.21c) but not on surfaces of hydraulically regenerated membranes (Appendix Figure A7.21b) suggesting that it was associated with reversible fouling alone through charge neutralization and NOM aggregation rather than cation bridging (Ahn et al. 2008). Therefore foulant-membrane bridging is attributed largely to aluminum (Sposito 1996).

Importantly, these spectral changes were significantly lower in the difference spectrum of the membrane after cycle-1. Therefore, these complexes appear to have been formed primarily between foulants in the source water and irreversibly bound foulants on the membrane surface at longer timeframes. This may explain the major role of acidic NOM fraction(Kim and Dempsey 2008, 2010) and metal-organic complexes(Yamamura et al. 2007a) in fouling reported earlier(Kim and Dempsey 2008). Bands in this spectral region could also signify minor contributions from non-carboxylic moieties comprising amide II (1570-1545 cm⁻¹), aromatic C=C stretching (1620-1580 cm⁻¹), and C-H deformation (1460-1378 cm⁻¹). Mechanisms of fouling following electroflotation pretreatment of Lake Houston water are discussed next.

4.3.3. Irreversible MF fouling in pretreated water (electroflotation-MF)

4.3.3.1. Irreversible accumulation of both hydrophilic and hydrophobic molecules over the entire duration of filtration

After cycle-1, both C-H (3050-2800 cm⁻¹) and O-H/N-H (3650-3100 cm⁻¹) bands on the membrane surface intensified compared to the virgin membrane (Figure 4.3 and Figure 4.4) in

pretreated water. Hence, unlike filtration of untreated source water, fouling appears to have been initiated by both hydrophilic and hydrophobic molecules after electroflotation. Further, more polar foulants including the $AI(OH)_3$ coagulant and non-proteinaceous organic compounds accumulated early on evidenced by the more prominent increase of O-H vibrations than C-H and no N and Si were detected after cycle 1 (Figure 4.2d).

Additionally, C-H bands intensified to a smaller extent than O-H bands from cycle-1 to cycle-5 (Figure 4.3). Therefore, similar to untreated water, hydrophilic molecules appear to have preferentially accumulated than hydrophobic foulants with successive filtration/regeneration over longer timeframes. The increased role of hydrophilic foulants during all stages of filtration in pretreated waters is attributed to the efficient removal of hydrophobic molecules by electroflotation (see next section) and the introduction of hydrophilic Al(OH)₃ precipitates. Importantly, higher regenerated fluxes were obtained after every cycle with electroflotation pretreatment even though more coagulant irreversibly accumulated on the membrane.

Mechanisms of irreversible Al accumulation were investigated by electrolyzing nanopure water pH 6.4±0.2 to generate the same 10 mg/L Al concentration used for pretreatment of Lake Houston water. Next, the suspension consisting of the "pure" coagulant in nanopure water was microfiltered and hydraulically regenerated as described in detail in Appendix section A3.8. New asymmetric (1580 cm⁻¹) and symmetric (1470, 1438, 1418 cm⁻¹) C(=O)O⁻ vibrations appeared in the FTIR spectrum for the membrane fouled by the pure coagulant. The asymmetric vibration was stronger than the symmetric stretching band indicating ligand exchange interactions (Gao et al. 2009, Nakamoto 2009) between the coagulant and the membrane surface. High resolution XPS also provided evidence for direct covalent/electrovalent interactions between the pure coagulant and the virgin membrane surface. O1s component peaks corresponding to $Al(OH)_{3(s)}$ shifted to lower binding energies (O-I 530.7 \rightarrow 530.4 and O-II 532 \rightarrow 531.8 eV), whereas that of

membrane shifted to higher binding energies (C(=O)OH/C(=O)OR 531.4 \rightarrow 531.8 and C-<u>O</u>R/C-<u>O</u>H 532.4 \rightarrow 532.9 eV). These are attributed to inner or outer sphere complexation of the coagulant (Alexander et al. 2001) with the membrane. Hence, both FTIR and high resolution XPS provided complementary evidence for coagulant complexation with carboxylate/carboxyl groups on the membrane surface.

4.3.3.2. Coagulant-mediated complexation of foulants with the membrane

Asymmetric (1650-1500 cm⁻¹) and symmetric (1500-1350 cm⁻¹) carboxylate stretching bands were significantly intensified in the difference spectrum of the irreversibly fouled microfilter operating on electroflotated water after cycle-1 and cycle-5 (Figure 4.4). Again, the $v_{as}C(=0)O$: $v_{s}C(=0)O$ intensity ratio increased compared to raw water spectrum indicating that flocs complexed with carboxylic/carboxylate groups on the virgin/fouled membrane surface. Further evidence for bridging/chelation was provided by the separation distance between symmetric and asymmetric $C(=O)O^{-}$ stretching bands (Gao et al. 2009, Nakamoto 2009) being in the range 120-220 cm⁻¹. Large changes in intensity even after cycle-1 compared with raw water demonstrate the importance of complexation of acidic functional groups to fouling initiation following pretreatment, unlike initial fouling during untreated water MF. This could arise from bridging of freely suspended or coagulated foulants mediated by dissolved aluminum hydrolysis products or bridging/chelation of the fresh Al(OH)₃ precipitates with carboxylic moieties on the virgin membrane surface. As shown in Figure 4.4, these bands further intensified after cycle-5 demonstrating continued complexation of carboxylic/phenolic groups with fouled membrane components over longer timeframes. Contribution of amide bands to these peak changes is minimal since only negligible amounts of nitrogen were detected on the membrane surface (Figure 4.2). Since electroflotation pretreatment increased efficiency of hydraulic regeneration (higher flux at the beginning of each cycle compared to untreated water) it appears that complexation predominantly contributed to coagulant accumulation on "inert" areas of the membrane surface with negligible pore penetration.

Changes in the elemental composition and chemical functionalities of irreversibly fouled microfilters operating on untreated and pretreated feed waters were rigorously linked to foulant transfer from the raw water to the electrochemically generated coagulant precipitates. The corresponding results are discussed next.

4.3.4. Foulant removal from source water during electrochemical pretreatment

Direct evidence that electroflotation pretreatment decreased concentrations of potential foulants in the feed water and subsequently on the membrane surface (Figure 4.4) was provided by FTIR (Figure 4.5) and XPS (Figure 4.2e) spectra of electrochemically generated flocs in the MF feed water. ATR-FTIR spectra of flocs floated to the water surface (orange line) and unfloated flocs still suspended in the water column (red line) formed during electrolysis of Lake Houston water are shown in Figure 4.5. Spectra of untreated surface water (blue line), and "pure" electrocoagulant generated in nanopure water (green line) are also superposed in Figure 4.5 to investigate the removal of organic acids, carbohydrates, proteins, and siliceous compounds during electroflotation.

Carbonyl peak of C(=O)OH groups (1730 cm⁻¹) significantly attenuated and $v_sC(=O)O^-$ (1416 and 1390 cm⁻¹) and $v_{as}C(=O)O^-$ (1550, 1532, and 1508 cm⁻¹) intensified in both floated and unfloated flocs with respect to raw water. Additionally, compared to the "pure" coagulant spectrum, symmetric (1480-1350 cm⁻¹) and asymmetric (1600-1500 cm⁻¹) COO⁻ stretching bands have emerged in the spectrum of electrofloated natural water indicating NOM-coagulant complexation (Guan et al. 2007, Lu et al. 1999, Omoike and vanLoon 1999) demonstrating effective removal of acidic organic molecules from the source water by electroflotation. The C-O, C-O-C, and Si-O bands (1260-840 cm⁻¹) were significantly broader in pretreated Lake Houston

water compared with the untreated source water (1200-950 cm⁻¹) and "pure" coagulant (1120-950 cm⁻¹). Similarly, the O-H peak also broadened from 3750-2750 cm⁻¹ in the source water and 3640-3125 cm⁻¹ in the "pure" coagulant spectra to 3750-2500 cm⁻¹ in the spectrum of the electrofloated natural water. This is due to reduced symmetry (Lu et al. 1999) of these moieties arising from the uptake of carbohydrate-like and siliceous compounds by Al(OH)_{3(s)}. Electrochemical treatment of surface water resulted in the appearance of amide I and amide II bands in the spectra of both floated and unfloated flocs conjoint with the appearance of Nsignals in XPS spectra (Figure 4.2e). Additionally, O-H/N-H stretching band broadened compared to electrolysis in nanopure water (3640-3125 cm⁻¹ \rightarrow 3750-3050 cm⁻¹) denoting the effective sorptive removal of proteinaceous compounds. These results show the sorption of carbonaceous, nitrogenous, and siliceous foulants onto Al(OH)_{3(S)} precipitates and complement XPS results (Figure 4.2e).



Figure 4.5. ATR-FTIR spectra of different MF feed suspensions. The spectrum of the electrofloated flocs collected at the top of the water surface during pretreatment is also shown.

Hydrophobic compounds were also removed by electrocoagulation of natural water as observed by increased intensity in the 3050-2800 cm⁻¹ region corresponding to C-H stretching

bands compared with "pure" coagulant in nanopure water in Figure 4.5. Bands at 3018, 2942, and 2856 cm⁻¹ were common to raw water and floated flocs suggesting efficient transfer of hydrophobic molecules to $Al(OH)_3$ precipitates that rose to the top of the electrochemical cell reducing their carryover to MF and subsequent sorption onto the membrane, thereby increasing flux. This also suggests greater affinity of hydrogen bubbles to floc surfaces due to their increased hydrophobicity (Stumm et al. 1992) following sorption of natural water constituents contributing to floc flotation. In contrast, C-H bands were not distinctly visible in the unfloated flocs that continued to be suspended in the water column suggesting their surfaces were relatively more hydrophilic. The intensification of O-H/N-H band in the flocs formed in natural water relative to untreated raw water is due to contribution from O-H vibrations of Al(OH)₃ precipitates (as seen in the significant hydroxyl peak in the "pure" coagulant spectrum). These comparisons demonstrate that electroflotation pretreatment removed several classes of potential foulants present in the surface water including acidic organic compounds (e.g., fulvic acids), hydrophilic organics (protein-like and carbohydrate-like substances), hydrophobic molecules (e.g., humic substances), and siliceous compounds thereby reducing their membrane surface concentrations and ultimately controlling fouling.

Substantial amounts of proteins (0.011 mg/mg Al), carbohydrates (0.035 mg/mg Al), and silicon (Adu-Wusu and Wilcox 1991) (0.001 mg/mg Al) were measured to be sorbed on electrofloated flocs by dissolving them at high pH (Tanneru et al. 2013). Additionally, DOC and specific UV absorbance (SUVA) reduced by 47% and 20% respectively following electroflotation-MF. In contrast, MF alone reduced DOC and SUVA by only 8% and 2% respectively. These bulk measurements validate FTIR results and show foulant transfer from raw water to flocs, which are removed from the MF feed water by flotation thereby reducing fouling.

4.4. Conclusions

During MF of untreated surface water, irreversible fouling of a modified PVDF membrane was largely initiated by hydrophobic molecules. Over multiple filtration/regeneration cycles, hydrophilic molecules progressively accumulated as the membrane got progressively coated with foulants. Irreversible fouling by carbohydrate-like, protein-like, and siliceous compounds was illustrated by their long-term accumulation even after repeated physical regeneration. Electroflotation pretreatment controlled fouling by (1) partitioning a fraction of NOM and siliceous compounds to the electrocoagulant thereby reducing direct foulant interactions with the membrane (2) floc flotation, which prevents a significant fraction of coagulant-bound foulants from reaching the membrane surface (Gamage et al. 2012) even though it significantly increased aluminum accumulation, and (3) forming large aggregates which decrease pore penetration (Gamage et al. 2012). Electroflotation reduced the concentration of hydrophobic molecules in the feed water but added $Al(OH)_{3(5)}$ causing polar molecules to contribute strongly to irreversible fouling over all time scales after pretreatment. Polyvalent aluminum coagulant species can bridge, chelate, or electrovalently complex foulants to membranes. This explains why coagulation pretreatment sometimes even increases fouling (Howe and Clark 2006b, Kimura et al. 2008) or only has a limited effect (Lahoussine-Turcaud et al. 1990a) and shows the importance of monitoring AI and Fe (Gu et al. 1994) concentrations in source/feed waters.

Foulants can undergo hydrogen bonding (Contreras et al. 2011, Yamamura et al. 2008) and hydrophobic interactions (Jucker and Clark 1994) with membranes. In addition to fingerprinting foulants (Chen et al. 2002a, Howe and Clark 2002b, Kim and Dempsey 2008, Lee et al. 2006, Tang et al. 2007, Vrijenhoek et al. 2001, Yamamura et al. 2007a, Yamamura et al. 2007b) FTIR and XPS provide clues to the nature of these chemical interactions since they are highly sensitive to perturbations in localized atomic environments that cause spectral peaks to

shift, broaden, and change in intensity (Little 1966, Nakamoto 2009, Urban 1993). We observed numerous peak shifts of C-H, O-H/N-H stretching vibrations and in the amide I region indicating compositional changes as well as chemical interactions between membrane surfaces and foulant molecules. For example in membranes fouled by untreated raw water, the C-H stretching bands blue shifted towards higher wave numbers with respect to the virgin membrane ($3022 \rightarrow 3025 \text{ cm}^{-1}$ and $2980 \rightarrow 2984 \text{ cm}^{-1}$ in Figure 4.3). This has been attributed to hydrophobic interactions of C-H groups with nearby polar moieties such as O-H groups (Schmidt et al. 2006). Additionally, membranes fouled by raw and pretreated waters depicted red shifts towards lower wave numbers of OH/NH bands compared to both virgin membrane (3715- $2600 \rightarrow 3700-2560 \text{ cm}^{-1}$ in Figure 4.3) and raw water (3750-2610 \rightarrow 3700-2560 cm $^{-1}$ in Figure 4.3). This can be attributed to hydrogen bonding of O-H groups with polar moieties such as OH, C=O, and N-H (Nyquist 2001a). Further, the amide I band in membranes filtering raw water after 5cycles red-shifted compared with the feed water (1654 \rightarrow 1650 cm⁻¹ and 1640 \rightarrow 1638 cm⁻¹ in Figure 4.4). This can possibly arise from hydrogen bonding of proteinaceous compounds, which lengthens peptide C=O bonds reducing their vibrational frequency (Schmidt et al. 2006). Multiple interaction modes can strengthen foulant attachment and magnify the extent of physically irreversible fouling. Such interactions will depend on NOM molecular weight (i.e., segment chain length) and functionalities, solution chemistry, and membrane surface composition partially explaining differences in fouling with source water origin, pretreatment, and membrane material (Howe and Clark 2002b, Laine et al. 1989, Wiesner and Laine 1996). Although this work provided clues to chemical bonding mechanisms between foulants and membrane surfaces, individual interfacial interactions during natural water MF could not be resolved due to severe peak overlap in IR spectra.

Chapter Five. Physicochemical Mechanisms of Cake Compression during (Electro)coagulation–Microfiltration of Surface Water

5.1. Introduction

A common method to reduce fouling and simultaneously remove organic matter during microfiltration (MF) and ultrafiltration (UF) is to pre-coagulate the feed water with hydrolyzing metal salts (Huang et al. 2009, Lahoussine-Turcaud et al. 1992, Wiesner et al. 1989a). An example is the 70MGD drinking water treatment plant in Columbia Heights, MN that pretreats Mississippi River water with ferric chloride. An alternative coagulant delivery technique is the in situ electrolytic dissolution of a metal anode, i.e., electrocoagulation. Since electrocoagulation is effective for contaminant removal (Cañizares et al. 2006a, Chen 2004, Vaghela et al. 2005, Zhao et al. 2010b, Zhu et al. 2005) and controlling MF/UF fouling (Ben Sasson and Adin 2010a, Gamage and Chellam 2011b, Gamage and Chellam 2013, Gamage et al. 2012, Timmes et al. 2009, Zhu et al. 2005) it may be a promising alternative to chemical coagulation especially for small systems. All real-world MF/UF membranes are operated at constant flux wherein the pressure is increased to compensate for flux loss due to fouling (Chellam and Jacangelo 1998a, Choi and Dempsey 2005). Although much work has focused on colloidal and organic fouling of low-pressure membranes (Chae et al. 2008, Choi and Dempsey 2004a, 2005, Howe et al. 2006), the factors controlling cake compression, induced by increasing transmembrane pressures necessary to maintain the design flux with the progression of fouling, has not yet been rigorously researched.

Cake compression research to date has largely focused on developing empirical constitutive equations relating permeability, specific hydraulic resistance, and porosity as a function of pressure (Sørensen and Sorensen 1997, Tiller and Kwon 1998, Tiller et al. 1987a).

The specific resistance of cakes (α) formed on membrane surfaces during water and wastewater treatment have been reported to increase in a power-law fashion with transmembrane pressure (Δ P) (Chellam et al. 1998b, Chellam and Xu 2006, Lee et al. 2005, Sørensen and Sorensen 1997),

$$\alpha^* = \alpha_0^* \Delta \mathsf{P}^{\mathsf{n}}, \tag{5}$$

where α_0^* denotes the specific resistance at null pressure, which depends on the macroscopic morphology of the overall cake (i.e., individual particle/aggregate size and aggregate shape and porosity) laid down at an asymptotically low stress ($\Delta P \rightarrow 0$). The compressibility index n quantifies the change in hydraulic resistance with pressure and depends on deformation and breakage of individual particles or aggregates. It is emphasized that although α_0^* and n have been empirically reported for several drinking- and wastewaters (Huang et al. 2011, Hwang et al. 2009, Iritani et al. 2007, Lee et al. 2000, Sioutopoulos and Karabelas 2012), more work is necessary to better understand physicochemical factors underlying compressibility of particulate structures formed on membrane surfaces.

The objective of this research is to rigorously and systematically elucidate physical and chemical factors contributing to compressibility of cakes formed during dead-end MF of untreated and pretreated surface water. Instantaneous MF flux profiles were measured over a range of pressures for Lake Houston water with no pretreatment and after alum and electrocoagulation pretreatment at two aluminum dosages. Insights into elastic compaction (i.e., floc deformation or rigidity) were obtained by determining crystallinity of precipitates using X-ray diffraction (XRD) and through microscopy. Physical parameters of colloids in MF feed waters were characterized in terms of size, ζ potential, and fractal dimensions. Elements present in the colloids present in MF feed waters, their chemical state and functionalities, and changes in peak location and area induced by changes in the electron density of their microenvironment

following (electro)coagulation were characterized using X-ray Photoelectron Spectroscopy (XPS) (Watts and Wolstenholme 2003).

5.2. Material and Methods

5.2.1. Source water quality

All experiments were performed using Lake Houston water sampled on January 14, 2012. The sample pH was 7.60±0.19, turbidity was 14.7±1.5 NTU, alkalinity was 71±2 mg/L as CaCO₃, calcium and total hardness were 48±3 and 51±3 mg/L as CaCO₃, and conductivity was 328±13 μ S/cm. Total iron, aluminum, and silicon concentrations were 0.07±0.03 mg/L, 0.21±0.04 mg/L, and 2.5±0.3 mg/L, respectively. Sulfate, nitrate, and nitrite concentrations in the raw water were 8 mg/L, 0.168 mg/L, and <0.01 mg/L respectively. NOM concentration (measured as dissolved organic carbon (DOC)) was 4.9±0.5 mg/L, and UV₂₅₄ absorbance was 0.143±0.005 cm⁻¹. The ζ potential was measured to be -17±2 mV.

5.2.2. Microfiltration

Constant pressure (14, 41, 83, and 164 kPa), unstirred, dead-end, MF was performed using modified PVDF membranes (0.22 μ m, 4.1 cm², GVWP02500 Durapore, Millipore). First 100 mL of nanopure water was passed through the virgin membrane followed by 300 mL of the feed suspension (raw water, electrochemically pretreated water, or alum coagulated water). Transmembrane pressure (TMP) (PX303-050G5V, Omega) and cumulative permeate volume (Ohaus Navigator N1H110, Fisher Scientific) were monitored digitally at a variable rate (0.05-1 Hz) to quantify instantaneous flux (Gamage et al. 2012). Following filtration, the cake was weighed after drying to a constant weight for 16 h at 35° C. All experiments were performed at pH 6.4±0.2.

5.2.3. Electrochemical and chemical (alum) coagulation

Electro- and alum coagulation parameters correspond to optimal conditions (10 – 15 mg Al/L and pH 6.4) that maximized MF fluxes (Gamage and Chellam 2011b, Gamage et al. 2012). Batch electrolysis experiments were conducted with a custom made 450 mL cylindrical Perspex cell which consisted of a Al anode (Puratronic, 99.9965% as Al, Alfa Aesar) concentric to a porous annular 316-stainless steel cathode. Galvanostatic electrolysis was performed at an initial pH of 6.4 with a current density of 20 mA/cm² for 93s (active anode surface area = 17.3 cm²) to generate the desired coagulant dose. The pH did not change substantially rising only to 6.6 at 10 mg/L and to 6.7 at 15 mg/L during electrochemical pretreatment. The entire suspension after electrolysis was gently mixed to resuspend all the flocs throughout the water column and microfiltered the entire suspension. Trivalent aluminum dissolved at near 100% Faradaic dissolution efficiency under these conditions (atomic absorption spectroscopy using Flame AA-AAnalyst 200). Electrode passivation was avoided by mechanically scrubbing and cleaning with dilute HNO₃ before each experiment.

Alum (ACS grade aluminum sulfate) chemical coagulation was performed using a programmable jar tester (PB-900, Phipps & Bird Inc.) with 60s rapid mixing at 300 rpm and 30 min slow mixing at 40rpm (velocity gradient = 32s⁻¹). After flocculation, the entire suspension was transferred to MF without sedimentation simulating the most common application of conventional coagulation pretreatment for MF/UF during municipal water and wastewater treatment.

5.2.4. XPS

X-ray spectra (PHI 5700 spectrometer) were obtained using monochromatic AI $K\alpha$ radiation (hv = 1,486.7 eV) incident at 90° relative to the axis of a hemispherical energy analyzer. MF feed water suspensions (raw Lake Houston water and (electro)chemically pretreated water) were vacuum dried for 48h and pressed on high purity indium substrates (99.9975% as In, Alfa Aesar) prior to analysis. Sample charging was controlled with the neutralizer. Survey spectra were obtained by sweeping over 0-1400 eV binding energy (BE) at a resolution of 0.8 eV/step for 5min at 187.85 eV band pass energy on a spot diameter of 1.1 mm. For the Au4f_{7/2} line, these conditions produced the full width at half-maximum (FWHM) of better than 1.6 eV. High-resolution spectra (step size = 0.1 eV) were obtained for photoelectrons emitted from C1s, O1s, N1s, Si2p, Al2p, and S2p at 23.5 eV pass energy and 45° take-off angle. For the Ag4f_{7/2} line, these conditions produced FWHM of better than 0.6 eV. The substrate's In3d_{5/2} (444 eV) peak served to internally standardize high resolution peak positions for elements of interest. Potential heterogeneities were accounted for by averaging 3-5 spectra from different regions of each sample. BE scale was calibrated using the Cu2p_{3/2} line at 932.62±0.05 eV and Au4f_{7/2} at 83.96±0.05 eV. Spectral smoothing, background subtraction, and curve fitting were performed using MultiPak (v5.0A) software (Physical Electronics Inc., MN).

5.2.5. XRD

Electro- and alum-coagulated flocs were separated through centrifugation, dried at ambient temperature for 24 h, and powdered before examining them by a X-ray diffractometer (Siemens D5000) equipped with a graphite monochromator. Isopropyl alcohol was used to uniformly coat samples on the zero background quartz sample holder. Diffraction patterns were collected using CuK α radiation (1.54056 Å) at 40 kV and 30 mA in the 2 θ scan range from 10° to 55° with steps of 0.02° 2 θ /s. Prior to sample analysis, instrument performance was verified with a quartz standard. The Joint Committee for Powder Diffraction Studies (JCPDS) database was used to interpret the diffraction patterns and identify the peaks.

5.2.6. Particle size, fractal dimension, and ζ potential

Effective size distributions of (electro)coagulated suspensions and raw water colloids in the range 0.05–900 μ m were measured by light scattering (He–Ne laser, $\lambda = 633$ nm, Mastersizer S, Malvern). Scattered light was measured at angles between 0.01° and 135° with a series of 42 angular detectors, 2 backscatter detectors, 2 alignment detectors and a center detector. Each measurement consisted of over 2000 sweeps (2 ms/sweep). Instrument performance was verified with highly monodispersed NIST-certified polystyrene latex beads of size 43 μ m and 92 μ m. Particle size distributions were obtained after aligning the optics and subtracting the background of nanopure water. Obscuration was maintained at 20% in each analysis to avoid multiple scattering. The measured intensity data were analyzed using Mie theory.

Mass fractal dimensions ($d_{f,3D}$) were measured using static light scattering (SLS, BI-200SM Brookhaven) equipped with a He–Ne laser (λ =632.8 nm) and a BI-9000AT correlator. Scattered intensities were recorded at 20° and 135° where a linear behavior was measured during preliminary experimentation (Gamage et al. 2012). An average of 3-5 separate measurements of each sample is reported.

The ζ potential was measured by monitoring the Doppler shift of a 632.8 nm He-Ne laser (Nicomp ZLS, Particle Sizing Systems, Santa Barbara, CA) at a fixed scattering angle of 14.7° under a 4 V/cm field strength and 0.4 cm electrode spacing. The average of 3-measurements is reported herein.

5.3. Results and Discussion

5.3.1. (Electro)chemical coagulation reduced fouling to a greater extent at lower

pressures

Instantaneous relative flux profiles for the two coagulant dosages at the lowest (14 kPa)

and highest (164 kPa) pressures investigated are shown in Figure 5.1 for raw (blue), electrocoagulated (red), and alum coagulated (green) Lake Houston water. Note that this manuscript focuses on the role of transmembrane pressure in inducing relative differences in fouling control rather than flux control by coagulation pretreatment, which has been the subject of numerous earlier investigations (Howe and Clark 2002a, 2006b, Laîné et al. 1990, Wiesner and Laine 1996). Importantly, fouling control by electro- and alum coagulation was significant only at the lowest pressure. At 14 kPa, the relative decrease in raw water flux at the end of the filtration cycle was 95%. Both types of pretreatment improved the pseudo steady-state relative flux substantially to ~75% and ~79% at coagulant dosages of 10 mg/L and 15 mg/L respectively (Figure 5.1a). In contrast, pretreatment only negligibly increased the pseudo steady-state relative flux at 164 kPa (from 99% decline for raw water to ~94% and ~96% for 10 mg/L and 15 mg/L and 15 mg/L coagulant dosages respectively). Hence, operating at a higher pressure considerably exacerbated fouling following (electro)coagulation pretreatment.

Increasing pressure from 14 kPa to 164 kPa had only a minor effect on the pseudo steady-state relative flux for the untreated water, decreasing it from 95% loss to 99% loss. However, pressure had a major effect on pretreated waters, i.e., the pseudo steady-state relative flux decreased from ~75% to ~94% for 10 mg/L coagulant dose and from ~79% to ~96% for 15 mg/L coagulant dose. Hence, pressure influenced fouling to a higher extent for pretreated MF feed suspensions compared to untreated Lake Houston water. Finally, the entire relative flux profile was highest for electrocoagulated suspensions at 14 kPa whereas an opposite trend was observed at 164 kPa where alum coagulation resulted in better fouling control. Although the differences were small they were highly reproducible with similar results generated by duplicate experiments.



Figure 5.1. Normalized instantaneous flux profiles corresponding to untreated (blue), electrocoagulated (red), and alum coagulated (green) Lake Houston water at (a) 10 mg/L and 14 kPa, (b) 10 mg/L and 164 kPa, (c) 15 mg/L and 14 kPa, and (d) 15 mg/L and 164 kPa. Entire length of each flux profile could be fitted with cake filtration model.

5.3.2. Flux profiles were quantitatively explained by a compressible cake filtration

model

The continuous curves in Figure 5.1 correspond to the classical cake filtration model (Hermia 1982a) demonstrating that cake filtration accurately and quantitatively governed the entire flux profile during MF of untreated and pretreated feed waters (Lee et al. 2003, Tiller 1990),

$$\frac{dt}{d(V/A_m)} = \frac{\mu \alpha^* C_b}{\Delta P} \left(\frac{V}{A_m} \right) + \frac{1}{J_0},$$
(6)

where t is time, V is cumulative permeate volume, A_m is the effective membrane area, α^* is the specific cake resistance on a mass basis, μ is the absolute viscosity, c_b is the bulk particle concentration, ΔP is the transmembrane pressure, and J_0 is the clean water flux. Figure 5.2 summarizes that in all cases, specific cake resistances increased with transmembrane pressure, i.e., compressible cakes were formed. Additionally, α^* was significantly higher for the raw water compared with pretreated suspensions and all cakes compressed in a power-law fashion (i.e., straight-line increase in α^* with ΔP in log-log scale).



Figure 5.2. Power law compressibility of colloidal deposits formed on the membrane surface for untreated Lake Houston water and for (electro)coagulated suspensions at (a) 10 mg/L and (b) 15 mg/L aluminum dosage.

As such, the raw water cakes can be classified as being moderately compactible (n=0.49) whereas highly compactible cakes were formed after pretreatment (0.61≤n≤0.83) (Tiller and Kwon 1998, Tiller et al. 1987a). A range of physical and chemical characteristics of the feed water suspensions (untreated, electrochemically pretreated, and alum coagulated water) were studied in more detail to rigorously investigate the underlying cake compression mechanisms.

5.3.3. Primarily amorphous Al(OH)_{3(s)} precipitates were generated by electro- and

chemical coagulation

Powder-XRD patterns of solids generated by alum addition (blue) and electrochemical aluminum addition (orange) to nanopure water are shown in Figure 5.1. Shallow and broad

peaks (hkl: 020, 120, 140, 031, 051, 200) were observed in the case of electrochemical coagulation indicating precipitation of small amounts of boehmite nanocrystals (Gamage and Chellam 2011b). An approximate 5nm crystal size was calculated based on the most intense peak (20=14.5°) using Scherrer's formula, which is in the size range of fresh Al precipitates reported earlier (Sposito 1996). Actual crystal sizes may be somewhat larger since microstrain (e.g., dislocations and stacking faults) and instrumental effects also contribute to peak broadening (Klug and Alexander 1974). The diffractogram of alum coagulated solids did not show any crystallinity indicating differences in the nature of precipitates formed by electro- and alum coagulation.

Diffractograms corresponding to Lake Houston water (black for waw water, red for electrocoagulation and green for alum coagulation) are also shown in Figure 5.3a. The only sharp peaks observed are from naturally occurring quartz (Gamage and Chellam 2011b) probably from clays. Distinct boehmite peaks obtained when Al was electrochemically added to nanopure water (orange line) were no longer visible in the corresponding diffraction pattern for Lake Houston water, which is attributed to disruption of crystalline Al precipitation by NOM (Masion et al. 1994, Newcombe and Dixon 2006a, Sposito 1996, Violante and Huang 1985). Hence, solids present in (electro)chemically treated MF feed waters were primarily amorphous (Berkowitz et al. 2005, Gamage and Chellam 2011b, Sposito 1996), also validated by the lack of crystal habit in electron micrographs (Appendix Figure A7.27b and c).

The atomic concentrations (%) of the untreated and (electro)chemically coagulated Lake Houston water as well as "pure" (electro)coagulants generated in nanopure water at pH 6.4 were obtained using XPS survey analysis and shown in Figure 5.3b. Results corresponding to "pure" precipitates generated in nanopure water will be discussed in this section and data for Lake Houston water will be discussed in §5.3.6.


Figure 5.3. a) XRD patterns of electrocoagulated and alum coagulated flocs. Diffraction patterns of raw water colloids and the precipitates generated in nanopure water are also shown. b) Oxygen, carbon, silicon, nitrogen, aluminum, and sulfur percentage atomic concentrations of MF cakes (untreated, electrofloated and alum coagulated Lake Houston water). Atomic concentrations corresponding to "pure" coagulants generated during nanopure water electroflotation and alum coagulation are also shown.

O:Al atomic concentration ratio corresponding to "pure" electrochemically generated coagulant in nanopure water was 3.14, indicating predominantly $Al(OH)_{3(s)}$ precipitates. Therefore, boehmite ($\gamma AlO(OH)$) did not contribute significantly to mass of Al solids even in nanopure water. A significantly higher O:Al ratio of 3.62 was obtained for "pure" alum-generated precipitates. Sulfur (3.29%) was detected on alum-generated flocs arising from the

concurrent addition of $SO_4^{2^-}$ anions along with Al (Letterman and Vanderbrook 1983). Adjusting for the contribution of $SO_4^{2^-}$ ions reduced the O:Al ratio to 2.96 showing that primarily $Al(OH)_{3(s)}$ was also precipitated during alum coagulation. Additionally, slightly higher particle sizes measured for alum coagulated flocs (Table 5.1) can be attributed to sulfate-mediated $Al(OH)_{3(s)}$ precipitation kinetics (Letterman and Vanderbrook 1983, Sposito 1996).

Amorphous precipitates in pretreated MF feed waters were gelatinous and fluffy when observed under the electron microscope (Appendix Figure A7.27d and e) unlike natural colloids in Lake Houston (Appendix Figure A7.27a and d). The gelatinous nature of amorphous Al(OH)₃ arises from kinetically-favored high water uptake, which eventually transforms to crystalline polymorphs with aging over several weeks or months (Berkowitz et al. 2005, Sato 1972). Hence, a portion of cake compressibility could be attributed to *elastic* deformation of individual flocs comprising the foulant layer on the membrane surface. This also partially explains the higher compressibility index measured after sweep flocculation compared with charge neutralization during MF of alum coagulated surface water (Lee et al. 2000). Crystalline quartz present in raw water and condensed siliceous shells (frustules) of diatoms (Tesson et al. 2009) are rigid and therefore not expected to deform at higher pressures partially explaining the lower compression index of cakes formed during MF of untreated water.

5.3.4. Physical characteristics of colloids in MF feed waters

Table 5.1 summarizes chemical and physical properties of colloids and flocs in the feed water and corresponding cakes. As expected, pretreatment significantly increased the foulant loading, and cake masses were similar following electro- and alum coagulation pretreatment. Greater productivity despite higher mass of cakes formed after pretreatment demonstrates the formation of more permeable deposits during MF of (electro)coagulated feed waters. This was confirmed by aggregation of natural colloidal matter during pretreatment (Appendix Figure A7.28) with alum and electrocoagulation forming similar-sized flocs for a given aluminum dose.

Hence, the lower specific resistance of cakes formed after pretreatment can be partly attributed

to larger particles being filtered.

Table 5.1. Feed water characteristics and cake parameters for the untreated Lake Houston water and after (electro)coagulation at 10 mg/L and 15 mg/L.

Cake parameters	Raw water	Electrocoagulation		Alum coagulation	
		10 mg/L	15 mg/L	10 mg/L	15 mg/L
Cake mass (mg/mL)	0.008±0.002	0.035±0.002	0.049±0.003	0.036±0.001	0.050±0.002
Particle size (μm)	14±3	175±12	188±14	186±10	194±13
ζ potential (mV)	-16.51±0.13	-1.21±1.22	2.61±0.56	-3.07±1.70	-0.19±1.27
d _{f/3D}	2.75±0.10	1.67±0.02	1.74±0.11	2.17±0.06	2.07±0.13
α_0^* (m/kgPa ⁿ)	4.00x10 ¹²	9.40x10 ⁹	4.39x10 ⁹	7.62x10 ¹⁰	4.23x10 ¹⁰
n	0.49±0.04	0.74±0.05	0.85±0.07	0.58±0.04	0.63±0.03
Comments on floc strength	Strongest	Weakest	Weakest	Medium	Medium
	个个hydrophobic	↑hydrophobic	个hydrophobic	↓hydrophobic	↓hydrophobic
Comments on	个个amides	√amides	√amides	↑amides	↑amides
chemical	个个acidic	↓acidic	↓acidic	个acidic	↑acidic
composition	organics	organics	organics	organics	organics
	个个silica	= silica	= silica	= silica	= silica

Suspended solids in untreated Lake Houston water were very dense ($d_{f,3D}$ =2.75), expected from low attachment efficiencies during reaction limited aggregation of stable, negatively charged colloids (Newcombe and Dixon 2006b). Electro- and alum coagulation effectively destabilized natural colloids by a combination of sweep flocculation and charge neutralization (Gamage and Chellam 2011b, Gamage et al. 2012) increasing attachment efficiencies and lowering fractal dimensions ($1.67 \le d_{f,3D} \le 2.17$). Formation of branched and porous flocs during electro- and alum-coagulation would further reduce specific cake resistance compared to increasing particle size alone. Note that subtle but reproducible differences in zeta potential were measured wherein alum coagulated flocs were always slightly more negative than their electrocoagulated counterparts for a given aluminum dose due to sorbed SO₄²⁻ ions (as discussed earlier in §5.3.3) (Letterman and Vanderbrook 1983). Hydrogen bubbles released at the cathode during electrocoagulation were readily incorporated into the flocs (Appendix Figure A7.29) further reducing their porosity compared with alum coagulation. Voids formed by hydrogen gas further decreased d_{f,3D} during electrocoagulation (e.g., 1.67 compared with 2.17 for alum coagulation at 10 mg/L dose). The higher porosity of individual electrocoagulated flocs can be expected to form more permeable cakes at null pressure (lower α_0^*) during MF after electrochemical pretreatment. Indeed, specific cake resistances at null stress were an order of magnitude lower for electrocoagulation pretreatment compared with alum coagulation for a given aluminum dose (e.g., 4.4 x 10⁹ and 4.2 x 10¹⁰ m/kgPaⁿ respectively at 15 mg/L dose). Increasing branching and porosity of electrocoagulated flocs can also be expected to reduce their strength inducing them to break and causing cake collapse as the transmembrane pressure is increased during MF of electrochemically pretreated waters. As expected, higher compressibility indices were measured during MF of electrocoagulated waters (e.g., 0.85 compared with 0.63 for alum coagulation at 15 mg/L dose). As seen in Figure 5.2, the specific resistances of electro- and alum coagulated cakes essentially overlapped at low pressure but diverged at higher pressures suggesting differences in *inelastic* compression mechanisms (i.e., cake collapse and migration of fines). These results are in line with the findings of a previous study where lower fractal dimensions generated more compressible cakes at higher pressures during MF of hematite floc-humic acid assemblages (Lee et al. 2005).

In addition to physical parameters discussed in this section, chemical factors leading to differences in cake compression for the two pretreatment types was investigated next.

5.3.5. Acidic organics, amides, and hydrophobic compounds were present on natural colloids (untreated water)

Cakes generated after filtering 300 mL of untreated Lake Houston water were vacuum

dried and analyzed by XPS. Survey spectra (Appendix Figure A7.30) showed that the major elemental constituents in Lake Houston water were carbon (C1s at 285 eV), oxygen (O1s at 532 eV), silicon (Si2s at 160 eV, Si2p at 103 eV), and nitrogen (N1s at 484 eV). Lower amounts of aluminum (Al2s at 119 eV, Al2p at 75 eV) and calcium (Ca2p at 348 eV) were also detected, which were validated by atomic absorption spectroscopy (0.2 mg/L and 0.4 mg/L respectively). The high resolution Si2p peak was centered near 103 eV showing predominantly oxygenated siliceous compounds (e.g., silica and silicates) in the Lake Houston water, which is consistent with quartz detected in XRD (Figure 5.3) and diatoms seen in SEM images. As discussed in §5.3.3, these forms of silica are rigid and therefore not expected to contribute to compressibility in the range of pressures employed in MF (<2 atm). Detailed core level spectral analysis was performed for C1s, O1s, and N1s peaks (Figure 5.4) to better characterize important NOM functionalities. The results revealed that NOM in Lake Houston contained protein-like, carbohydrate-like, hydrophobic, and acidic organic compounds as explained below.



Figure 5.4. Curve fitted high resolution XPS spectra corresponding to C1s, O1s, and N1s core level analysis of raw water colloids present in the MF cake layer.

The C1s core level spectrum was resolved into four component peaks with FWHM = 1.3-1.7 eV and BEs at i) 284.95 eV attributed to -<u>C</u>-C-/-<u>C</u>-H in aromatic and aliphatic hydrocarbon backbones of NOM, ii) 286.76 eV attributed to -<u>C</u>-O-/-<u>C</u>-N-in alcohols, phenols, and proteins, iii) 288.58 eV attributed to -<u>C</u>=O/-O-C-O- in aldehydes, ketones, amides, acetals, and hemi-acetals, and iv) 289.25 eV attributed to <u>C</u>(=O)OH/<u>C</u>(=O)OR in humic and fulvic acids and esters (Badireddy et al. 2010, Crist 2005, Echlin 1984, Gamage et al. 2012, Naumkin et al. 2012). The shake-up satellite peaks at 293.2 eV and 296.08 eV probably resulted from π - π * transitions of aromatic rings (Echlin 1984) indicating aromaticity of natural organic matter present in Lake Houston water. As seen in Figure 5.4, the O1s core level peak was decomposed into three peaks each with FWHM=1.7 eV and BEs at i) 531.68 eV attributed to carbonyl groups present in carboxyl/carboxylate (C(=<u>O</u>)OH/ C(=<u>O</u>)O⁻), ester (C(=<u>O</u>)OR), and amide (C(=<u>O</u>)N) moieties, ii) 532.65 eV attributed to <u>O</u>-(C, H) from hydroxide, acetal, and hemiacetal, and iii) 533.72 eV attributed to single bonded oxygen present in carboxyl (C(=O)<u>O</u>H) and ester (C(=O)<u>O</u>R) groups (Badireddy et al. 2010, Chung 2001, Crist 2005, Echlin 1984, Watts and Wolstenholme 2003). Acetal, hemiacetal, and hydroxide indicate the presence of carbohydrates and free sugars whereas carboxyl/carboxylate moieties are symptomatic of organic acids.

The N1s peak was centered around 400.2 eV demonstrating predominantly organic nitrogen (Moulder et al. 1995), which was verified by very low concentrations of nitrite (<0.01 mg/L) and nitrate (0.16 mg/L) measured via ion chromatography. Raw water N1s core level spectrum was resolved into two component peaks with 1.0-1.2 eV FWHM (Figure 5.4) and BEs at i) 400.12 eV attributed to -<u>N</u>-C-/-<u>N</u>-H in amines and amino acids, and ii) 400.93 eV attributed to -<u>N</u>(C=O)- in amides. Protein-like substances were measured by the modified Lowry assay to be 0.24 mg/L.

Significant amide, acidic, and hydrophobic moieties in natural colloids suggests presence of hydrogen bonding, complexation, and hydrophobic interactions increasing their overall strength and reducing their compressibility index. Changes in the component peak locations and areas with reference to untreated Lake Houston water shown in Figure 5.4 were used to identify NOM sorption onto coagulated flocs as discussed in §5.3.6.1 and 5.3.6.2. Changes in the atomic composition of precipitates formed during electro- and alum coagulation of Lake Houston water are discussed next.

5.3.6. Transfer of Lake Houston water constituents to flocs

Figure 5.3b also provides evidence for the transfer of carbonaceous, siliceous, and nitrogenous compounds from the raw water to (electro)chemically precipitated coagulants. For example, Si and N were not detected in "pure" coagulants generated in nanopure water, but increased to 3.1% and 2.1% respectively in electrochemically precipitated Al(OH)₃ and to 3.0% and 2.7% respectively in alum coagulated Lake Houston water. Similarly, only 9.3% and 5.1% of adventitious carbon were detected by electrolyzing or adding alum to nanopure water respectively. However, C atomic concentration in the flocs formed in Lake Houston water increased to 32.3% after electrochemical treatment and to 26.6% after alum coagulation. Further, survey spectra showed that alum coagulation was more effective in removing nitrogenous compounds as observed by higher N percentages measured in chemically (alum) precipitated flocs in Lake Houston water compared with electrochemically precipitated flocs. In contrast, both the uptake and speciation of sorbed siliceous compounds were very similar for electro- and alum coagulated flocs as shown by survey scans and high resolution Si2p peak deconvolution (Appendix Figure A7.31). Therefore, measured differences in cake characteristics with pretreatment type probably arose from other elements.

The aluminum composition of alum- and electrolyzed Lake Houston flocs was similar (11.6%). However, O was slightly higher in alum coagulated Lake Houston flocs (56%) compared with those generated electrochemically (51%). Similar to "pure" coagulants discussed earlier, this is attributed to oxygenated groups (e.g., SO_4^{2-}) present following alum addition as evidenced

by (i) slightly more sulfur in flocs compared with untreated lake water (0.4% and 0.2% respectively in Figure 5.3b) and (ii) marginally more negative surface charge on flocs formed by adding alum to lake water compared with electrochemical treatment of lake water (§5.3.4).

5.3.6.1. Uptake of carbonaceous compounds by flocs

Figure 5.5 depicts curve fitted high resolution C1s XPS spectra corresponding to MF feed waters; raw Lake Houston or no pretreatment (left panel), electrocoagulation (middle panel), and alum coagulation (right panel). The alum coagulation C1s peak was similar in intensity compared with electrochemical pretreatment showing both pretreatment methods removed similar amounts of organic carbon. As expected, similar DOC concentrations were measured in MF permeates following alum coagulation (2.5 mg DOC/L at 10 mg/L and 2.3 mg DOC/L at 15 mg/L) and electrochemical pretreatment (2.6 mg DOC/L at 10 mg/L and 2.4 mg DOC/L at 15 mg/L). Areas of C-C/C-H, C-N/C-O, C=O/O-C-O, and C(=O)OH/C(=O)OR component peaks changed in (electro)coagulated flocs compared with untreated lake water indicating differences in the accumulation of respective moieties based on coagulation type. The C-C/C-H component peak area was higher in electrocoagulated flocs (51.5%) compared with alum flocs (42.7%) (see also Table A7.2). Hence, electrocoagulated flocs sorbed hydrophobic organic compounds to a greater extent compared with alum coagulation (Tanford 1991), presumably mediated by hydrogen bubbles released during electrolysis which show greater affinity towards hydrophobic surfaces (Ducker et al. 1994, Gamage and Chellam 2013, Stumm et al. 1992). Slightly lower UV₂₅₄ absorbance values were detected after electrocoagulation pretreatment (0.054 cm⁻¹ at 10 mg/L and 0.049 cm⁻¹ at 15 mg/L) compared with alum coagulation (0.059cm⁻¹ at 10 mg/L and 0.054 cm⁻¹ at 15 mg/L) confirming greater uptake of hydrophobic compounds by electrochemically generated precipitates.



Figure 5.5. Deconvoluted XPS C1s spectra corresponding to MF feed water flocs after no pretreatment, electrochemical pretreatment (includes both floated and suspended flocs/ electrocoagulation), and alum coagulation. Magnitude of y axis (intensity) is same in all three graphs.

In contrast, C(=O)OH/C(=O)OR peak area was higher in alum coagulated flocs (5%) than in electrocoagulation (3.7%) indicating better uptake of acidic organic matter by Al(OH)_{3(s)} generated during chemical coagulation. Additionally, compared with raw water, the C(=O)OH/C(=O)OR peak was shifted by +0.67 eV in electrochemically generated flocs and by +0.55 eV in alum coagulated flocs indicating potential inner-sphere complexation of carboxylated moieties present in Lake Houston water with coagulant =Al-OH groups (Alexander et al. 2001, Crist 2005, Guan et al. 2007). ATR-FTIR analysis of electrocoagulants also shows complexation of acidic organic matter onto flocs (Gamage and Chellam 2013). Further, C-N and C=O/C(=O)N component peak areas were higher in alum coagulated flocs (36.6% and 14.2% respectively) compared with electrocoagulation (33.8% and 11.1% respectively) showing its greater affinity towards nitrogenous compounds such as amides. None of the C1s component peaks of flocs (except C(=O)OH/C(=O)OR) exhibited significant BE shifts compared with raw water demonstrating largely physiorption of organic compounds onto Al(OH)_{3(s)}.

5.3.6.2. Uptake of nitrogenous compounds by flocs

Deconvolution of N1s core level spectra of electrochemically pretreated and alum

coagulated flocs showed peaks corresponding to N-(C=O) and N-C/H moieties indicating sorption of proteinaceous compounds (Figure 5.6 and Table A7.3). The N-C/H component peaks in flocs showed negligible shifts in BE compared with raw water (<0.25 eV) indicating physisorption of amines onto both types of coagulants. In contrast, the N(C=O) peak showed greater shifts (+0.59 eV for electrocoagulation and +0.41 eV alum coagulation) signifying amides were more strongly sorbed than amines. Moreover, stronger and greater binding of proteinaceous compounds to alum coagulated flocs was inferred because the corresponding N-(C=O) peak was more intense (area = 21.1%) than electrocoagulated aggregates (area = 17.9%).



Figure 5.6. Curve fitted XPS N1s spectra corresponding to MF feed water flocs after no pretreatment, electrochemical pretreatment (includes both floated and suspended flocs/ electrocoagulation), and alum coagulation. Magnitude of y axis (intensity) is same in all three graphs.

An additional peak at lower BEs than the <u>N</u>-C/H peak of untreated Lake Houston water (400.02 eV) was observed for alum coagulation (399.2 eV) and electrocoagulation (399.5 eV). Further, the corresponding area of this new peak was greater for alum coagulated flocs (31.2%) than for electrocoagulation (24.1%). This, coupled with the greater intensity of the overall N1s peak (Figure 5.6) as well as <u>C</u>-N and N(<u>C</u>=O) component peaks (Figure 5.5) observed for alum coagulation than electrocoagulation further corroborates greater removal of nitrogenous compounds by alum coagulation. Colorimetric protein measurements on flocs after dissolving

them at high pH, also revealed higher concentrations on alum coagulated flocs (14 ng proteins/mg Al) compared with electrocoagulation (10 ng proteins/mg Al).

5.4. Implications for Floc Strength, Inelastic Compression, and Membrane

Operation

As seen in Figure 5.5, C-C and C-H peaks contributed the most to the C1s core level spectrum in both electro- (52%) and alum-coagulated (43%) flocs denoting the preferential (approx. 50%) removal of hydrophobic components of natural organic matter such as humic material during coagulation (Croué et al. 1999, Dempsey 2006). Hydrocarbon backbones demonstrate the presence of hydrophobic moleties on flocs that are capable of non-polar (e.g., hydrophobic) interactions, which were important determinants of the strength of aggregates formed in both types of pretreatment. However, such interactions are relatively weaker than hydrogen bonding and complexation (Erbil 2006). Alternately, concentrations of amides, carbonyls, and carboxyl were higher on alum coagulated precipitates (57%) than in electrocoagulation (48%). Since amides are strong hydrogen bond donating/accepting groups (Aleman et al. 1995, Grabowski 2006, Karshikoff 2006) and acidic organic moieties facilitate complexation (e.g., bridging) (Alexander et al. 2001, Crist 2005, Guan et al. 2007), alum coagulated flocs were subject to stronger interparticle attractive forces thereby making them more cohesive. In other words, since concentrations of polar groups were lower on electrochemically generated precipitates, they can be expected to more easily rupture at higher applied pressures than flocs conventionally generated using alum. These flocs will also be more easily surface eroded by fluid shear detaching smaller particles from the flocs. Hence, collapse of individual aggregates accompanied by movement of fines into available void spaces due to greater porosity and lower strength of the flocs appears to be more important during MF of electrocoagulated Lake Houston water. We therefore hypothesize that a more stratified cake is

formed on the membrane filtering electrocoagulated water wherein the layer nearest the membrane is comprised of most densely packed particles (least permeable) and the permeability increases away from the membrane surface (Tiller and Kwon 1998) . (In)elastic cake compression provides the mechanistic basis of very high fouling rates reported when the transmembrane pressure is increased to maintain a constant flux during dead-end MF (Chellam and Jacangelo 1998a, Choi and Dempsey 2005). In other words, greater water productivity is expected by filtering at a constant pressure and bringing more membranes on-line as fouling reduces flux. These findings need to be confirmed at pilot-scale and capital and operating costs need to be estimated before a particular mode of operation (i.e., constant flux or constant pressure) can be recommended for large-scale plants.

Chapter Six. Conclusions and Recommendations for Future Work

6.1. Conclusions

Aluminum electrochemical pretreatment successfully controlled MF fouling during forward filtration of surface water primarily by forming more permeable cake layers. Electroflotation further enhanced fluxes compared with electrocoagulation by lowering both the foulant mass loading and the cumulative hydraulic resistance. Hence, this work underscores the importance of utilizing flotation inherent to electrochemical treatment for better control of fouling.

Flux reduction during MF of untreated and (electro)chemically pretreated Lake Houston water quantitatively obeyed cake filtration theory during the entire course of filtration. Hence, fouling was primarily caused by deposition of natural colloids, macromolecules, and coagulated materials on the membrane forming a surficial cake layer thereby increasing frictional losses for water permeation. Therefore, for surface waters with relatively high suspended solids concentrations and for coagulated suspensions, cake filtration theory is sufficient to model short-term flux decline between backwashes as was recommended in several earlier reports (Chellam et al. 1998a, Kim and DiGiano 2006). However, this may not always be the case for MF of low turbidity waters where a distinct pore blocking phase controls short-term fouling (Bagga 2007, Bagga et al. 2008b).

XPS and ATR-FTIR analysis of irreversibly fouled PVDF membrane surfaces after MF provided direct evidence for the irreversible attachment of proteinaceous, carbohydrate-like, acidic, and siliceous compounds present in surface waters. FTIR analysis showed that proteinaceous compounds exhibit a greater irreversible fouling potential compared with carbohydrate-like compounds. However, since carbohydrate-like compounds are more

abundant in surface water sources than proteinaceous compounds, their total or absolute contribution to irreversible fouling can still be higher.

Since it is difficult to synthesize a membrane material with universally low fouling potential for the entire spectrum of NOM components, we propose that the best approach to control organic fouling is through reduction of direct contact between NOM molecules and the polymer matrix of the membrane. NOM enmeshment, complexation, and uptake by aluminum precipitates reduce direct interactions of its functional groups with the membrane. Electroflotation pretreatment has an added advantage in this regard compared to conventional coagulation methods, since it removes a significant fraction of coagulant-bound-NOM during pretreatment itself not allowing it to reach the membrane surface. This reduces the probability of loosely-coagulant-bound foulants from depositing on the membrane. However, the coagulant itself can irreversibly accumulate on the membrane surface forming inner- and outer-sphere complexes as revealed by FTIR spectra of physically regenerated PVDF membranes following MF of electrofloated lake water. This suggests mechanisms by which "chemically enhanced" backwashes incorporating acids and chelating agents improve foulant removal along with operational fluxes in full-scale installations.

Compared with alum coagulated flocs, electrocoagulated flocs were weaker due to a more branched morphology, higher porosity, and decreased presence of functional groups such as amides and acidic organics that are capable of relatively stronger specific interactions (i.e., hydrogen bonding and complexation). Hence, inelastic compression caused by collapse of individual aggregates accompanied by movement of fines into available void spaces appears to be more important during MF of electrocoagulated Lake Houston water at higher pressures. Consequently, a more stratified cake is hypothesized to be formed after electrocoagulation compared with alum coagulation, wherein, the layer nearest the membrane is highly resistant to

water permeation being comprised of smaller particles and the permeability increases away from the membrane surface. Since (in)elastic cake compression increases the transmembrane pressure required to maintain a constant flux during dead-end MF, greater water productivity is expected by filtering at a constant pressure and bringing more membranes on-line as fouling reduces flux.

Aluminum electrochemical pretreatment is recommended as an alternative for conventional chemical coagulation for both short- and long term fouling control of low-pressure membranes. However, since large scale MF/UF applications universally operated at constant flux, greater compressibility of electrochemically generated flocs can worsen fouling compared with chemical coagulation. Therefore, for electrochemical coagulation to be implemented as a pretreatment step for real-world MF/UF applications, operating conditions such as pH, current density, and electrode geometry should be optimized for inherent floc flotation.

It is emphasized that our observations should be cautiously extrapolated to real world systems for fouling control since different trends might be obtained for other types of membranes, source water chemistries, and operating conditions. Hence, to obtain results of direct relevance to actual membrane applications, longer term experiments using continuous flow electrochemical reactors and pilot-scale tests will need to be performed for a given membrane-feed water combination.

6.2. Recommendations for Future Work

The following suggestions could potentially build on the research described in this dissertation.

Fouling investigation

Physically irreversible fouling mechanisms were examined in detail only for raw and electrofloated Lake Houston water. Understanding how different microenvironments of surface

water after subjecting to electrocoagulation and alum coagulation will affect physically irreversible fouling control, will aid in better evaluation of electrochemical pretreatment as an alternative to conventional coagulation.

For example, instantaneous flux profiles over five filtration/regeneration cycles were obtained (ΔP = 14 kPa) for raw, alum coagulated, and electrocoagulated Lake Houston water (Figure 6.1). Results revealed that (1) initial and final fluxes of a given cycle continued to decrease with the number of cycles in all cases suggesting increasing irreversible accumulation of foulants, (2) both pretreatment methods reduced physically irreversible fouling compared with no pretreatment, and (3) conventional chemical coagulation with alum better improved flux after physical regeneration compared with aluminum electrocoagulation.



Figure 6.1. Instantaneous flux profiles over 5 filtration and hydraulic regeneration cycles for raw (untreated) water (blue), and pretreated (red – electrocoagulated and green - alum coagulated) Lake Houston water respectively. The dotted lines denote irreversible fouling ($\Delta P = 14 \text{ kPa}$).

Foulant-membrane and foulant-coagulant interfaces have already been carefully probed using ATR-FTIR and XPS and the results are currently being analyzed. These results will provide information on the mechanisms of irreversible attachment of foulants to the membrane surface after each pretreatment method. Analysis of chemical cleaning solutions of irreversibly fouled membranes to quantify different types of potential foulants such as aluminum, silica, proteins, and carbohydrates (Gamage and Chellam 2013) will also aid in corroborating conclusions drawn via spectroscopy. A similar approach can be used to investigate mechanisms of chemically irreversible fouling and fouling control after (electro)coagulation pretreatment.

During the investigation of the mechanisms of cake compression in (electro)coagulation–MF of surface water, the measured physical properties (e.g., ζ potential, particle size, fractal dimension) corresponded to colloids and aggregates present in MF feed suspensions. Examining these properties of the cake itself after subjecting to different pressures will provide more direct evidence of physical mechanisms behind cake compression.

Lower DOC removals were observed when alum coagulated lake water was subjected to sedimentation prior to MF (40%), than in direct filtration of coagulated suspensions (~50%). Additionally, MF cakes generated after alum coagulation contained greater amounts of amides carboxyl groups. Hence foulant coated flocs appeared to have acted as a secondary membrane resulting in greater sorption of different types of NOM molecules. Measurement of interaction forces between the foulant coated flocs and molecules of known chemistry (e.g., amides and carboxyl groups) using atomic force microscopy will aid in better understanding of the mechanisms behind greater sorption of amides and organic acids by foulant coated alum coagulated flocs.

Investigation of electrode fouling

SEM micrographs of fouled aluminum electrodes revealed long term electrocoagulation operation resulted in electrode fouling (local passivation and pitting corrosion, Figure 6.2). Electrode fouling remains a major drawback of electrochemical processes limiting their largescale implementation (Holt et al. 2005). For electrocoagulation/flotation-MF process to be

viable in large scale, it is important to understand the mechanisms involved in electrode fouling and investigate methods to control it.



Figure 6.2. SEM micrographs of fouled aluminum anode after 60 min of electrolysis at pH 6.4 and 20 mA/cm² current density, (a) passivation due to formation of oxide/hydroxide layer, (b) pitting corrosion.

Microscopic (optical and electron) and spectroscopic (XPS and ATR-FTIR) methods are useful in investigating the chemical mechanisms of pitting corrosion and passivation (Badawy et al. 1999, Cai et al. 2013, Goverde et al. 2012, Mesquita et al. 2012). For example, metallurgical and electron microscopy can be used for morphological analysis whereas XPS can be used for surface composition and depth profile analysis of pits/ passivation layers of the fouled anode. Additionally, investigation of the effect of common anions present in water and wastewater applications (e.g., Cl⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻) on electrode fouling mechanisms will also provide valuable insights into better understanding of electrode passivation.

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Appendices

A1. Supporting Information for Chapter Two



A1.1. Raw water quality

Figure A7.1. Summary of Lake Houston water quality parameters for the sample collected on December 14, 2009.

A1.2. Scanning electron micrograph of raw water constituents



- *Figure A7.2. Scanning electron micrograph (SEM) of natural colloidal matter present in the raw water.*
- A1.2. Image processing for particle size measurement.



Figure A7.3. Optical microscope image of flocs formed at 5 mg/L AI and 6.4 pH and the corresponding thresholded image (top row). The bottom row corresponds to electrocoagulation at 15 mg/L AI and pH 6.4.

Quality assurance.

Mann-Kendall values were all approximately equal to 0.5 for all the water quality parameters measured for our particular Lake Houston water sample revealing any no statistically significant (α = 0.05) temporal trends in the data. This coupled with consistency of water quality parameters described in §2.2.1 of the main paper demonstrate that the water sample did not deteriorate over the course of this study. Additionally, approximately 20% of the experiments at different pH, coagulant dosage, and pressures were repeated. Paired t-tests conducted on instantaneous relative flux values from duplicate experiments showed no statistical differences at the 95% confidence level. Three examples of statistically similar flux decline profiles under different feed water pH, applied pressures, and aluminum concentrations are shown in Figure A7.5.



Figure A7.4. Reproducibility of specific cake resistances measured for various pressures, feed water pH, and aluminum dosages over the entire duration of this study.

Figure A7.4 summarizes that very similar cake specific resistances, α^* (described in §2.3.4) were measured from all duplicate experiments. The coefficient of divergence (a self-normalizing parameter) of α^* was calculated to be 0.121 for pH 7.5, 0.097 for pH 6.4, and 0.111

for the entire dataset indicating very low spread between repeated experiments. Paired t-tests and Wilcoxon signed-rank tests also revealed no statistical differences between duplicate experiments at the 95% confidence level. These results demonstrate that all our laboratory protocols related to coagulation, flocculation, and MF were consistent and highly reproducible thereby allowing a quantitative comparison of results generated over the entire duration of experimentation.



Figure A7.5. Duplicate normalized flux profiles under different aluminum dosages, filtration pressures, and pH conditions.



Figure A7.6. Comparison of aluminum concentrations measured by atomic absorption spectrometry (AAS) and inductively coupled plasma – mass spectrometry (ICP-MS). Note that a novel technique recently developed in our labs was employed for this purpose (Danadurai et al. 2011).

A2. Supporting Information for Chapter Three

A2.1. Image analysis for particle size determination and fractal dimension analysis



Figure A7.7. Image based a) floc size analysis was done using cellSens Dimension software, b) fractal dimension analysis done using box counting technique using ImageJ software.

A2.2. Quality control and quality assurance.

Approximately 25% of the experiments at different coagulant dosages and pressures were repeated. Paired t-tests conducted on instantaneous relative flux values and pH values from duplicate experiments showed no statistical differences at the 95% confidence level. Examples of duplicate flux decline profiles for raw, electrocoagulated and electrofloated waters corresponding to different pressures and aluminum concentrations are shown in Figure A7.10. Figure A7.8 illustrates that very similar cake specific resistances, α^* were measured from duplicate experiments. The coefficient of divergence of α^* was calculated to be 0.091 where as that of k_i was 0.072 indicating very low spread between repeated experiments. Paired t-tests and Wilcoxon signed-rank tests also revealed no statistical differences between duplicate experiments at the 95% confidence level. The high consistency and reproducibility of our results allow comparison of experiments performed over the 11 month period of this study.



Figure A7.8. Reproducibility of specific cake resistances and intermediate blocking parameters measured for different pressures and aluminum dosages with electrocoagulation and electroflotation pretreatment.



Figure A7.9. X-ray diffraction patterns obtained for flocs of lake water electrofloated at 10mg/L.



Figure A7.10. Normalized flux profiles of repeated experiments corresponding to different dose/ pressure combinations, a) $\Delta P = 13.8$ kPa, raw water, electrocoagulation pretreatment at 10 mg/L, b) $\Delta P = 13.8$ kPa, 163.6 kPa, electroflotation pretreatment at 10 mg/L.

A2.3. pH changes during electrochemical pretreatment.

The pH showed a noticeable variation with time during electrocoagulation and the final pH was always greater than the initial pH (Figure A7.11). Several studies have reported similar increases in final pH. This pH increase can be due to, (i) hydrogen evolution at the cathode which results in formation of OH⁻ ions, (ii) even though OH⁻ ions participate in aluminum hydroxide precipitation, anions like Cl⁻ and SO₄²⁻ present in the lake water can partly exchange

with OH^{-} in $Al(OH)_{3}$ which can release OH^{-} back to the solution increasing the pH, (iii) CO_{2} is over saturated in acidic pHs and hence can be released due to H_{2} bubbling resulting in pH increase.



Figure A7.11. Change in final steady state pH after electrochemical pretreatment of raw water.



Figure A7.12. Improvements in relative permeate flux only up to an intermediate value of aluminum dosage (10 mg/L) at a constant transmembrane pressure of 13.8 kPa following electrocoagulation pretreatment (a). Worsening fouling with increasing pressure during electrocoagulation - microfiltration (b).



Figure A7.13. Optical images of raw water, electrocoagulated MF feed suspensions, electrofloated MF feed suspensions and electrofloated supernatants.



Figure A7.14. Raw water microfiltration intermediate blocking followed by cake filtration and cake filtration dominating in almost entire duration of microfiltration of 10 mg/L electrocoagulated and electrofloated water (inset).



Figure A7.15. Comparison of cake parameters between electrocoagulation and electroflotation, a) effects of increasing aluminum electrocoagulant dosage: on total cake resistances at a fixed transmembrane pressure (13.8 kPa), ;b) power law compressibility of colloidal deposits formed on the membrane surface at 0 mg/L (control) and at optimum aluminum dose (10 mg/L).

A2.4. Experimental details of electrocoagulation and electroflotation



Figure A7.16. Schematic of apparatus used for electrocoagulation and electroflotation experiments.

Steps involved in electroflotation process:

- 1. Adjustment of pH from 7.6 to 6.4 using 0.1N HCl.
- 2. Electrolysis of the feed water at high mixing speed for a predetermined time period.
- 3. Stop applying current and slow mix the solution further for two minutes.
- 4. Drain water from the bottom of the cell and transfer for microfiltration.

Steps involved in electrocoagulation process:

- 1. Adjustment of pH from 7.6 to 6.4 using 0.1 N HCl.
- 2. Electrolysis of the feed water at a high mixing speed for a predetermined time period.
- 3. Stop applying current and mix the entire solution further for two minutes at high speed so that all the flocs (including the floating ones) would suspend in the solution.
- 4. Transfer all the water for microfiltration.

A3. Supporting Information for Chapter Four



A3.1. Schematic of electroflotation experimental setup

Figure A7.17. Schematic of electroflotation cell used in the experiments.

A3.2. XPS data analysis

Table A7.1. Calculation of % atomic concentration of elemental O foulants present on the
membrane surfaces (pretreated and untreated) corresponding to cycle 1, 3, and 5.
Atomic concentrations were adjusted to minimize contributions from the virgin
membrane(Riviáere and Myhra 1998). Here, O concentration of the virgin membrane
after multiplying by the F concentration ratio between fouled and virgin membrane
surfaces (F/F_{virgin} where $F_{virgin} = 28.80$) was subtracted from that of the fouled
membranes.

Cycle	O _{fo} +mem	ulant brane	C _{fo}	ulant Ibrane	I	-	F/F	virgin	O _{foul} O _{fou} +mem F/F _v O _{vi}	lant = ulant brane - irgin X rgin	C _{foul} C _{fou} +mem F/F _{vi} C _{vi}	lant = ulant Ibrane - irgin X rgin
	Raw	EF	Raw	EF	Raw	EF	Raw	EF	Raw	EF	Raw	EF
1	16.66	19.97	54.85	51.93	26.83	25.36	0.93	0.88	3.05	7.12	2.14	2.10
3	19.57	24.56	52.19	47.81	23.60	22.09	0.82	0.77	7.60	13.37	5.82	4.41
5	21.36	26.54	50.36	45.36	21.49	20.39	0.75	0.71	10.47	16.20	8.15	5.29

Carbon, Fluorine and oxygen contents of the virgin membrane were 56.59%, 28.8% and 14.6% respectively.

One set of example calculations are presented next. Here, since oxygen was present in both the foulants and the virgin membrane, fluorine signal which was absent in the foulants was used to adjust the contribution of oxygen from the virgin membrane (Riviáere and Myhra 1998). In the case of no pretreatment cycle 5 (raw), following steps were followed when adjusting O contribution from the virgin membrane.

- 1. Calculate the ratio between F concentrations on the fouled membrane and virgin membrane ($F_{fouled}/F_{virgin} = 21.49/28.80 = 0.75$).
- Multiply the calculated ratio by % atomic concentration of O on the virgin membrane (14.60) which is the contribution of O from the membrane itself (0.75x21.36=10.95).
- 3. Subtract the contribution of O from the membrane from the total O concentration measured from the fouled membrane (21.36) which is the O contribution from the foulants only (21.36-10.95=10.41) or "virgin membrane adjusted O concentration".
- 4. Divide the "virgin membrane adjusted O concentration" by the C concentration of the fouled membrane (50.36) which is the "virgin membrane adjusted O/C ratio"

(10.41/50.36=0.2067).

Table A7.2. % atomic concentrations of N, Al, Si, O, and C detected on the irreversibly fouled membrane surfaces corresponding to pretreated and untreated cases for cycle1, 3, and 5. Since C and O had contributions from both the virgin membrane and from the foulants, their concentrations were adjusted to minimize the contribution from the virgin membrane (see Table A7.1).

Cycle	N		A	Al	S	i	(C		C
	Raw	EF	Raw	EF	Raw	EF	Raw	EF	Raw	EF
1	0.14±	0.00	0.53±	2.57±	0.68±	0.00	2.83±	7.12±	2.31±	2.10±
1	0.02	0.00	0.08	0.19	0.06	0.00	0.19	0.23	0.14	0.13
2	0.80±	0.10±	0.71±	4.84±	2.48±	0.65±	7.60±	13.37±	6.15±	4.41±
5	0.12	0.03	0.14	0.08	0.09	0.15	0.50	0.57	0.45	0.13
E	1.65±	0.17±	0.87±	5.92±	3.51±	1.06±	10.13±	16.20±	8.81±	5.29±
5	0.20	0.03	0.07	0.18	0.26	0.03	0.55	0.04	0.51	0.33

 Table A7.3. % atomic concentrations of source water, lake water after electroflotation (in floated floc layer, suspended flocs, and floated + suspended flocs), and "pure" coagulant formed by electrolyzing nanopure water. Concentrations corresponding to virgin membrane surface are also shown.

Sample		С	Ν	Al	Si	0	F	Ca	Cl	Na	In
Source water		43.71	2.94	1.89	6.67	40.39	0.34	1.28	0.51	1.50	0.76
	floate d flocs	29.18	1.84	12.49	1.81	53.68		0.56			0.47
Electrof loated	Suspe nded flocs	36.48	2.15	10.41	4.21	46.05		0.11			0.54
raw water	floate d + suspe nded flocs	32.83	1.99	11.45	3.01	49.36		0.34			0.51
"Pure" co	agulant	9.47		21.48		67.69					1.35
Virgin me	mbrane	56.59				14.60	28.80				

Table A7.4. Atomic concentration ratios of source water, lake water after electroflotation, "pure" coagulant formed by electrolyzing nanopure water, and virgin membrane surface.

	N/C	Al/O	Si/C	AI/C	0/C
Source water	0.07	0.05	0.15	0.04	0.92
Electrofloated	0.06	0.22	0.00	0.36	1.52 (~1.06 from coagulant
raw water	0.00	0.25	0.09		assuming Al:O=1:3)
"Pure "coagulant	0	0.32	0	2.25	7.15
Virgin membrane	0	0	0	0	0.26

Table A7.5. Organic and Al concentrations present in feed waters and amounts desorbed fromthe irreversibly fouled membranes using HCl (pH 2) and NaOH (pH 12) after cycle 1and cycle 5 in the presence and absence of pretreatment.

	Untre	eated (Raw w	ater)	E	ectrofloate	d
Paramet er	MF Feed concentra tion (mg/L)	Desorbed foulants - cycle 1 (mg/cm ²)	esorbed Desorbed ulants - foulants - cycle 1 cycle 5 ng/cm ²) (mg/cm ²)		Desorbed foulants - cycle 1 (mg/cm ²)	Desorbed foulants - cycle 5 (mg/cm ²)
Al	0.21 ± 0.04	N/A	0.001± 0.001	3.10 ± 0.05	0.002 ± 0.001	0.010 ± 0.002
Al(OH)₃ (using Al:O=1:3)	N/A	N/A	0.003	~9.3	~0.006	~0.03
DOC	5.013 ± 0.4	0.011 ± 0.005	0.068 ± 0.01	3.031 ± 0.2	0.007 ± 0.003	0.038 ± 0.008
DOC + Al(OH) ₃	N/A	~0.011	~0.071	N/A	~0.013	~0.068

A3.2. FTIR analysis

A3.2.1. FTIR peak assignments

Table A7.6.	Peak assignments for FTIR spectra (Boccaccio et al. 2002, Chen et al. 2002a, Lin-Vien
	1991, Mantsch and Chapman 1996, Nakamoto 2009, Nyquist 2001a, b, Stuart 2004)
	(v - stretching vibrations, δ - bending vibrations).

Peak Position (cm ⁻¹)	Peak Assignment
900-680	fingerprint region, ring breathing
695	N-H wagging
780, 798	Si-O-Si intertetrahedral bridging bond vibrations
850-680	vAl-O
798, 780	Si-O-Si intertetrahedral bridging bond vibrations
820-750	glycosidic linkages of polysaccharides
872	δC-Η, δC-F
1100-950	AI-O-AI
1200-900	vC-O-C/ vC-O carbohydrates, ring vibrations
~1040	vC-O-C n-acetyl amino sugars in bacterial cell wall
1152	v_{as} C-O-C, ring vibrations
1100	vSi-O amorphous (Si-O-Si)/biogenic silica (Si-O-C)
1184	vC-H, v _s C-F
~1215	vC-C , vC-H , v_{as} C-F
1280-1255	νφ-OH (phenol), Amide III (vC=N + δN-H)
1280-1250	δC-OH of COOH and φ-OH
1314	δOH (primary, secondary), ν _{as} C-O-C (ester)
1340	δOH (tertiary, phenolic)
1500-1300	ν _s C(=O)O ⁻
1480-1400	vN-CH ₃
1460-1378	δС-Н
1510-1450	vC=C-C ring vibrations
1570-1545	Amide ΙΙ (<u>δΝ-Η</u> + νC-Ν)
1700-1500	v _{as} C(=0)0 ⁻
1650-1590	δOH of water
1620-1580	vC-C aromatic
1700-1600	Amide I (<u>vC=O</u> + δC-N + δN-H)
1755-1700	v _{as} C(=O)OH, vC(=O)OR, vC=O (humics, lipids, fatty acids)
2750-2610	hydrogen bonded vOH of COOH
3000-2850	vC-H aliphatic
3050-3000	vC-H aromatic
3400-3050	vN-H from amino acids, proteins, and amino sugars
3750-3300	vO-H from carbohydrates, alcohols, Al-O-H, and Si-O-H

A3.2.2. Use of FTIR data to interpret interactions leading to membrane fouling

ATR-FTIR spectroscopy can be used in tandem with XPS analysis to identify foulants and to interpret interactions leading to physically irreversible fouling through changes in the prominent peaks of the functional groups responsible for, i) hydrogen bonding (frequency shifts towards lower wave numbers/ red shifting of O-H/N-H band of IR spectrum at 3800-2500 cm⁻¹) (Grabowski 2006), ii) complexation interactions (attenuation of C=O stretching vibration at~1730-1720 cm⁻¹ and intensification of C(=O)O⁻ stretching bands in the 1800-1300 cm⁻¹ region where the intensity of asymmetric vibration (1700-1550 cm⁻¹) is greater than that of symmetric band (1500-1380 cm⁻¹) (Little 1966, Nakamoto 2009), and iii) hydrophobic interactions (intensity changes together with frequency shifts towards higher wave numbers/ blue shifting of C-H stretching bands in the 3050-2800 cm⁻¹ region which indicates the interactions of C-H groups with neighboring polar molecules providing indirect evidence for hydrophobic interactions) (Schmidt et al. 2006, Tanford 1991).

Minor variations in the characteristic group vibrational frequencies arises as a result of local differences in molecular environment, either because of intra-molecular interaction between groups in the molecules, or intermolecular interaction with the surroundings (Little 1966). These spectral changes can be used to investigate the interactions between a foulant moiety and its environment (e.g., virgin or foulant coated membrane). For example, weak interactions of foulant functional groups (e.g., O-H/N-H band, C-O-C band, amide I band) with Al(OH)₃ precipitates/ foulants/ membrane reduce their symmetry, activating vibrational modes which were otherwise inactive, hence leading to wider range of vibrational energies which broadens the IR peaks (Little 1966) of foulant sorbed flocs/ fouled membrane surface spectra compared with the spectrum of non-bonded sample (e.g., clean precipitates/ feed water/ virgin membrane). On the other hand, hydrogen bonding between O-H groups of foulants and

membrane can stretch the O-H bond hence reducing its IR vibrational frequency compared to non-hydrogen bonded O-H groups (virgin membrane/ clean precipitates). This leads to red shifting of the OH/NH band which can be observed by its low frequency tail (i.e., greater intensity in the lower frequency side of the peak- \rightarrow 3400-2500 cm⁻¹) compared with nonhydrogen bonded virgin membrane or raw water spectra. Similarly, hydrogen bonding of C=O moiety of the peptide groups of proteins can stretch the C=O bond reducing its vibrational frequency. Hence red shifting of amide I band of fouled membrane spectrum compared with raw water spectrum indicates possible hydrogen bonding of C=O groups of proteinaceous foulants with the membrane surface. Cation mediated ligand exchange interactions (e.g., bridging) of carboxyl moieties of foulants with the carboxyl groups on the membrane surface lead to attenuation of C=O band of C(=O)OH groups due to deprotonation of the carboxyl groups and increase the intensity of symmetric and asymmetric carboxylate bands. Similarly, electrovalent or electrostatic interactions of carboxylate groups also change the intensity of symmetric and asymmetric C(=O)O⁻ bands.

Table A7.7 summarizes the spectral changes observed in this study in the regions associated with hydrogen bonding and hydrophobic interactions along with their interpretations (see Figure 4.3).

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Spectrum	Vibration	Spectral change (cm ⁻¹)		Interpretation	
Figure 4.2: Raw water cycle 1	vC-H	Blue shift compared with virgin membrane	3022→3025, 2980→2984	Hydrophobic interactions/ interactions of C-H groups with polar moieties of virgin membrane	
Figure 4.2:		Red shift compared with raw water	3750-2690→ 3720-2660	Hydrogen bonding between	
cycle 1		Red shift compared with virgin membrane	3760-2720→ 3720-2660	the virgin membrane	
Figure 4.3: Raw water		Red shift compared with raw water	1654→1650 1640→1638	Hydrogen bonding of	
cycle 1	VC=O	Peak broadening compared with raw water	1565-1540→ 1580-1520	with the virgin membrane	
Figure 4.2: Raw water cycle 5	vC-H	Blue shift compared with virgin membrane	3022→3025, 2980→2984	Hydrophobic interactions/ interactions of C-H groups with polar moieties of foulant coated membrane	
Figure 4.2: Raw water cycle 5	vO-H/N-H	Red shift/greater intensity compared with raw water cycle 1	3720-2660→ 3700-2645	Greater extent of hydrogen bonding with successive cycling	
Figure 4.2: Pretreated water cycle 1	vC-H	Blue shift compared with virgin membrane	3022→3025, 2980→2984	Hydrophobic interactions/ interactions of C-H groups with polar moieties of virgin membrane/coagulant	
Figure 4.2: Pretreated		Red shift compared with raw water	3750-2690→ 3680-2680	Hydrogen bonding of uncoagulated and coagulated foulants and	
water cycle 1	vO-H/N-H	Red shift compared with virgin membrane	3760-2720→ 3680-2680	Al(OH)₃ precipitates with the virgin membrane surface	
Figure 4.2: Pretreated water cycle 5	νС-Н	Blue shift compared with virgin membrane	3022→3025, 2980→2984	Interactions of virgin membrane C-H groups/C-H moieties of foulants with the surface hydroxyl groups of the coagulated flocs	
Figure 4.2: Pretreated water cycle 5	vO-H/N-H	Greater red shift/ intensity compared with electrofloated water cycle 1	3680-2680→ 3660-2625	Hydrogen bonding of uncoagulated and coagulated foulants and Al(OH) ₃ precipitates with the foulant coated membrane surface	

 Table A7.7. List of IR spectral changes associated with hydrogen bonding and hydrophobic interactions of foulants with the membrane surface.

A3.4. Particle size distributions



Figure A7.18. Particle size distributions of MF feed solutions in the presence and absence of electroflotation pretreatment.

Compared to untreated Lake Houston water, % volume size distribution of the feed solutions after electroflotation shifted to right corresponding to greater particle sizes (Figure A7.18). This shows that electroflotation increased the particle size of the colloids present in Lake Houston water (i.e., volume-based mean particle size: $23.28\pm3.18 \mu m \rightarrow 73.96\pm7.11 \mu m$).

A3.5. Composition of raw water contaminants

Raw water IR spectrum depicted in Figure A7.19 shows presence of protein-like, carbohydrate-like, humic-like, as well as siliceous compounds in Lake Houston water. The higher wavenumbers (3750-3300 cm⁻¹) of the broad band centered around 3380 cm⁻¹ comprises of O-H stretching vibrations of alcohols and phenols whereas the lower wavenumbers (3400-3050 cm⁻¹) correspond to N-H stretching of amines and amides as well as O-H stretching of carboxylic acids. This band also has contributions from Si-OH stretching vibrations as was confirmed by presence of Si-O-Si stretching vibrations at 780-800 and ~1100 cm⁻¹, in tandem with the Si2p signal in XPS analysis. Symmetric (2850 and 2990 cm⁻¹) and asymmetric (2916 and 3045 cm⁻¹) alkyl and

aromatic C-H stretching vibrations accompanied by C-C skeletal vibrations (1350-1000 cm⁻¹) and C=C-C aromatic stretching vibrations (1615-1580 and 1510-1450 cm⁻¹) are indicative of hydrocarbon backbone and aromatic rings of humic substances.

The collective presence of amide peaks at 1700-1600, 1570-1545, 1300-1200, 3400-3050, and 725-670 cm⁻¹ arising from amide I, amide II, amide III, N-H stretching, and N-H wagging bands accompanied by N1s XPS signal confirm the presence of proteinaceous foulants (Lin-Vien 1991, Stuart 2004). Additionally, glycosidic (1200-1000 cm⁻¹) and N-CH₃ (1480-1400 cm⁻¹) vibrations can be attributed to n-acetylamino sugars. Comparable results were reported by Lee at al. for isolated algal organic matter and surface water colloids (Lee et al. 2006). Presence of carbohydrates were confirmed by the large broad peak at 1200-1000 cm⁻¹ (vC-OH: 1116, 1060 cm⁻¹, and vC-O-C: 1137, 1168, 1150 cm⁻¹) along with the -OH band at 3750-3300 cm⁻¹.

A3.6. Increasing accumulation of foulants on the irreversibly fouled membrane surfaces

Normalized FTIR spectra of membrane surfaces after cycles 1 and 5 are shown in Figure A7.2 for raw (solid blue cycle-5, dashed blue cycle-1) and electrofloated (solid red cycle-5, dashed red cycle-1) feed waters. Band intensities corresponding to carbohydrate-like (vO-H 3750-3300 cm⁻¹, vC-O-C/vC-O 1200-900 cm⁻¹, vC-O-C 820-750 cm⁻¹), proteinaceous (vN-H 3400-3050 cm⁻¹, vC=O/vNH₂ 1650 cm⁻¹, vN-H/vC-N 1540 cm⁻¹, vC-O-C 1036 cm⁻¹), humic-like (vC-H 3050-2800 cm⁻¹, vC=C-C 1510-1450 cm⁻¹, v(C=O)O⁻ 1700-1300 cm⁻¹), and siliceous (vSi-O-H 3750-3300 cm⁻¹, vSi-O-Si 1100 cm⁻¹, 800 cm⁻¹, and 780 cm⁻¹) increased from cycle-1 to cycle-5. As seen in Figure A7.2, regions corresponding to O-H (3650-3200 cm⁻¹) and Al-O (850-680 cm⁻¹) stretching vibrations significantly intensified even after cycle-1 both in the spectra corresponding to raw water and treated water suspensions. The intensity further increased for cycle-5 demonstrating progressive Al(OH)_{3(s)} coagulant accumulation on pretreated-membrane surfaces.



Figure A7.19. FTIR spectrum of source water with the second derivative spectrum showing the presence of carbohydrate-like, proteinaceous, humic-like and siliceous compounds of NOM.



Figure A7.20. ATR-FTIR spectra of virgin membrane (green line), irreversibly fouled membrane surfaces operating on electrofloated water (solid red: cycle 5, dotted red: cycle 1), and untreated Lake Houston water (solid blue: cycle 5, dotted blue: cycle 1).

A3.7. XPS survey spectra of source water constituents, irreversibly fouled membrane and cake



Figure A7.21. XPS survey spectra of (a) Lake Houston water, (b) membrane surface after source water filtration/regeneration cycle 5, and (c) cake layer after filtration of 150 mL of Lake Houston water in the absence of pretreatment.

XPS survey spectrum of raw water constituents revealed the presence of O, C, Al, Ca, Na, N, and Si (Figure A7.21a). Fe2p signal was absent in this spectrum due to its low concentration (0.07±0.03 mg/L). As observed in Figure A7.21b, Ca was absent on the irreversibly fouled membrane surface even after the fifth filtration/regeneration cycle of source water filtration suggesting negligible complexation with the membrane. However, Ca2p signal was detected in the cake layer formed during forward filtration of Lake Houston water which was hydraulically

layer

removed during backwashing (Figure A7.21c) suggesting Ca²⁺ ions predominantly contributed to reversible fouling (Ahn et al. 2008).

A3.8. Evidence for direct coagulant-membrane interactions

A control experiment was performed to investigate direct coagulant-membrane interactions leading to irreversible fouling, in the absence of other foulants present in natural water. In this experiment, nanopure water was electrolyzed to generate the same 10 mg/L AI concentration used in electroflotation pretreatment of Lake Houston water. Next, the suspension consisting only of the "pure" coagulant was microfiltered and hydraulically regenerated prior to FTIR and XPS analysis. Figure A7.22 depicts the IR spectrum of the "pure" coagulant precipitates generated in nanopure water (dotted green line) along with the difference spectrum of irreversibly fouled membrane after filtering this coagulant suspension (solid green line).

Emergence of new asymmetric (1580 cm⁻¹) and symmetric (1470, 1438, 1418 cm⁻¹) COO⁻ vibrations where greater relative intensity of asymmetric vibration in the spectrum corresponding to pure coagulant fouled membrane (solid green line) compared to unfiltered "pure coagulant" spectrum (dotted green line) in Figure A7.22 shows inner-sphere complexation between carboxylate groups on the membrane surface and the "pure" aluminum coagulant. Formation of more than one type of coordination complex was evidenced by the appearance of multiple symmetric and asymmetric bands. Their separation distances (Δv) varied between 110 and 170 cm⁻¹ indicating both chelating and bridging complexation of the coagulant with the membrane surface (Gao et al. 2009, Kang and Xing 2007, Nakamoto 2009). Clues to "Pure" coagulant – membrane inner-sphere complexation was also observed by O1s (top panel in Figure A7.23) and C1s (bottom panel in Figure A7.23) core level analysis, which showed peak shifts and emergence of new peaks. These envelopes were fitted using the positions relative to

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the F1s peak of the membrane at 686.6 eV (in virgin and fouled membrane spectra) and Al2p peak at 74.4 eV (in "pure" coagulant spectrum). For example, O1s peaks in the irreversibly fouled membrane after filtration/regeneration of the coagulant in nanopure water showed that component peaks corresponding to the coagulant shifted to lower binding energies (O-I 530.7 \rightarrow 530.4 and O-II 532 \rightarrow 531.8 eV), whereas that of membrane shifted to higher binding energies (C(=O)OH/C(=O)OR 531.4 \rightarrow 531.8 and C-OR/C-OH 532.4 \rightarrow 532.9eV). Moreover, an additional peak emerged between the coagulant peaks and membrane peaks at 531.7 eV corresponding to the carboxylate groups inner-spherically complexed (Alexander et al. 2001) with the virgin membrane surface. C1s spectra also provided evidence for inner-sphere complexation of carboxylic groups with the coagulant wherein the virgin membrane peak at 288.20 eV has shifted to lower binding energies by 0.34 eV (to 287.86 eV) in the membrane surface fouled by the "pure" coagulant (Guan et al. 2007) (Bottom panel in Figure A7.23).



Figure A7.22. ATR-FTIR difference spectra of coagulant in nanopure water and the membrane surface after filtering 100 mL of the "pure" coagulant suspension and hydraulically regenerating it.



Figure A7.23. Spectra of coagulant and membrane in a control experiment. Top panel: XPS O1s core level spectra of virgin membrane, "pure" coagulant, and irreversibly fouled membrane following filtration of the "pure" coagulant suspension. Bottom panel: XPS C1s core level spectra of virgin membrane and irreversibly fouled membrane after filtration of the "pure" coagulant suspension.



Direct microfiltration of untreated surface water

Figure A7.24. Proposed conceptual model for irreversible fouling after raw water and electrofloated water.

A4. Supporting Information for Chapter Five

A4.1. Duplicate experiments showing electrocoagulation improved flux better than alum coagulation at 14 kPa and the trend reversed at 164 kPa



Figure A7.25. Duplicate experiments of electrocoagulation and alum coagulation corresponding to 10 mg/L and a) 14 kPa and b) 164 kPa.





Figure A7.26. Dominant cake filtration for almost the entire duration of MF of untreated and pretreated water, a) 10 mg/L and 14 kPa, b) 10 mg/L and 164 kPa.

A4.3. Electron micrographs of cakes generated after filtering untreated Lake Houston water,



and (electro)coagulated lake water

Figure A7.27. Scanning electron micrographs (SEM) of raw water colloids showing presence of diatoms in Lake Houston water, MF cake generated after electrocoagulation pretreatment of lake water and nanopure water (15 mg/L, 14 kPa), c) MF cake generated after alum coagulation of lake water and nanopure water (15 mg/L, 14 kPa).

Al(OH)_{3(s)} precipitates generated during both pretreatment methods provide nucleation sites for micro- and macro-flocs formation during sweep flocculation leading to better flocculation of colloids during pretreatment. In addition to sweep flocculation, raw water colloids appear to have destabilized through charge neutralization as indicated by more neutral ζ potentials observed after both pretreatment methods (§5.3.2). Hence, under the dosing regimen used in this study, it can be concluded that colloids were primarily destabilized through charge neutralization and sweep flocculation during both types of pretreatment methods (Benjamin and Lawler 2013). A4.4. Optical microscopy images of the raw water colloids and flocs generated during electrochemical and chemical coagulation pretreatment of lake water



Figure A7.28. Phase contrast optical microscopy images of particles/flocs present in Lake Houston water and pretreated (alum coagulated and electrochemically treated) suspensions.



Figure A7.29. Electrochemically generated flocs consisting of hydrogen bubbles.

A4.5. Raw water XPS survey spectrum showing presence of different elemental foulants in the

MF cake layer



Figure A7.30. XPS survey spectrum of raw water colloids present in the MF cake.

A4.6. Elemental composition of MF cakes generated after raw water, (electro)coagulation of

lake water, and (electro)coagulation of nanopure water filtration

Table A7.8. Percentage atomic concentrations of cakes formed after filtering untreated,
electrocoagulated, and alum coagulated Lake Houston water. Results corresponding
to "pure" coagulants formed by electrolyzing and alum coagulating nanopure water
are also shown

Sample	С	N	AI	Si	0	S
Source water	44.43	2.96	1.86	6.71	43.96	ND
Electrocoagulated flocs	32.32	2.06	11.63	3.18	51.02	ND
"Pure "coagulant - Electrocoagulation	9.26	ND	22	ND	68.69	ND
Alum coagulated flocs	26.58	2.68	11.67	2.61	55.97	0.4
"Pure "coagulant - alum coagulation	5.08	ND	19.84	ND	71.8	3.29

Table A7.9. Percentage areas and positions of component peaks obtained after curve fitting high resolution C1s core level spectra of untreated cakes corresponding to raw water, electrochemically- and alum- coagulated lake water. The corresponding curve fits are shown in Figure 4b Figure 5.

Accignment	Р	eak Positior	1	% Area			
Assignment	Raw	EC CC		Raw	EC	CC	
С-С, С-Н	284.95	285.08	284.97	49.94	51.5	42.71	
C-OH,C-N	286.76	286.68	286.52	33.01	33.77	36.62	
C=O, O-C-O	288.58	288.36	288.3	7.09	11.06	14.17	
C(=O)OH, C(=O)OR	289.25	289.82	289.92	2.01	3.67	5.04	
satellite	293.2			5.03			
satellite	296.08			2.92			

Table A7.10. Positions and percentage areas of component peaks obtained after curve fitting high resolution N1s core level spectra of cakes corresponding to untreated raw water, electrochemically conditioned, and alum coagulated lake water. The corresponding curve fits are shown in Figure 6.

Accignment	P	eak Positio	on	% Area			
Assignment	Raw	EC	CC	Raw	EC	CC	
NI		399.5	399.23		24.12	31.23	
NII	400.02	400.27	400.3	66.85	58.02	43.35	
NIII	400.83	401.42	401.24	33.15	17.85	21.1	

Table A7.11. Positions and percentage areas of component peaks obtained after curve fitting high resolution Si2p core level spectra of untreated raw water constituents, electrochemically conditioned, and alum coagulated raw water. The corresponding curve fits are shown in Figure A7.31.

Accignment	Р	eak Positio	n	% Area			
Assignment	Raw	EC	CC	Raw	EC	CC	
Si I	103.05	102.88	102.74	84.5	75.26	72.96	
Si II	103.94	104.38	103.81	15.5	24.74	27.04	

A4.7. Uptake of siliceous compounds by flocs



Figure A7.31. Curve fitted XPS Si2p spectra corresponding to MF feed water flocs after no pretreatment, electrochemical pretreatment (includes both floated and suspended flocs/ electrocoagulation), and alum coagulation. Magnitude of y axis (intensity) is same in all three graphs.

Corroborating the XRD and electron microscopy results, Si2p peak of raw water generated cake was centered near 103 eV indicating colloidal siliceous matter present in Lake Houston water mainly existed in oxygenated forms (e.g., silica and silicates). Deconvoluted high resolution Si2p peak (Figure A7.31, raw) revealed two component peaks, where the one at 103.05 eV-attributed to silica and silicates, mainly contributed to the overall peak (84.5%). The smaller peak at 103.94 eV is also attributed to a different polymorph of silica (Naumkin et al. 2012).
Similar to untreated Lake Houston water, the Si2p high resolution spectra of pretreated flocs were also resolved into two component peaks with BEs at (i) 102.74 eV (the primary peak) attributed to silica/silicates and (ii) 103.81 eV attributed to SiO₂ (Figure A7.31). Additionally, both the peaks intensities and the relative areas of the component peaks were comparable in electrocoagulation and alum coagulation. Hence, the degree of sorption and speciation of the sorbed siliceous compounds seem to be largely similar in both cases.

A5. Comparison of Electroflotation and Alum Coagulation-Sedimentation for MF

Fouling Control



Figure A7.32. Normalized instantaneous flux profiles corresponding to no pretreatment, electroflotation, and alum coagulation-sedimentation of Lake Houston water at (a) 10 mg/L, 14 kPa, and pH 6.4.

In order to investigate how the floc flotation observed in electrochemical pretreatment compared with floc sedimentation typically practiced in conventional chemical coagulation, instantaneous flux profiles corresponding to electroflotation-MF and alum coagulation-MF were monitored. The corresponding cake masses and the permeate water quality in terms of DOC and UV₂₅₄ were also measured.

Figure A7.32 summarizes the normalized instantaneous flux profiles corresponding to no pretreatment, electroflotation, and alum coagulation-sedimentation at the optimum coagulation conditions observed in previous experiments for MF fouling control (pH 6.4, 10 mg/L and 14 kPa). Both pretreatment methods significantly improved MF flux compared with untreated raw water. Additionally, the extent of improvement was largely similar in both methods as was observed by nearly overlapping flux profiles (Figure A7.32). MF cake mass corresponding to electroflotation (0.0136 mg/mL) was approximately 25% higher than that corresponding to alum coagulation-sedimentation (0.0107 mg/mL). However, the specific cake resistance corresponding to electroflotation (8.97x10¹² m/kg) was lower than that in alum coagulation-sedimentation (1.17x10¹³ m/kg) suggesting electroflotation-MF cake layer was more permeable. Hence, the adverse effect of greater foulant mass being transferred to the membrane seems to have been counteracted by more permeable cake structure generated in electroflotation-MF. Additionally, electroflotation-MF removed more organics (DOC 55%, UV₂₅₄ 65%) than alum coagulation-sedimentation-MF (DOC 40%, UV₂₅₄ 61%).

A6. Miscellaneous Experimental Details



Computerized data acquisition

Figure A7.33. Schematic of the apparatus used for bench scale MF experiments.

LabVIEW data acquisition

Automatic data acquisition for flux, pressure, and temperature was performed using a program written in LabVIEW (version 8.6, National Instruments, Austin, TX, USA) at a variable rate of 0.05-1 Hz. A digital weighing balance (Ohaus Navigator N1H110, Fisher Scientific, Houston, TX, USA) recorded the cumulative permeate mass. A pressure transducer having a readable range of 0.5-5.5V (PX303-200G5V, Omega Engineering Company, Stamford, CT) was employed to continuously monitor the pressure of the feed water. The temperature of the feed

tank was monitored using a probe (TJ120CPSS116S, Omega Engineering Company, Stamford, CT) having a readable range of 0-200°C.



Figure A7.34. Calibration curve of the pressure transducer (left) and pressure profiles obtained during five different constant pressure, dead-end MF experiments (right).

Data acquisition systems (LabVIEW) records voltage signals form pressure, transducer, and temperature probes. Therefore, the signals were converted to physical experimental parameters such as pressure and temperature using calibration curves. Figure A7.34 shows the calibration curves of both pressure and temperature with good correlation coefficients (r^2 >0.99).

Figure A7.35 shows the user interface (front panel) of the LabVIEW program used for instantaneous mass, pressure, and temperature data collection at a desired frequency.



Figure A7.35. Front panel of the LabVIEW program used for instantaneous mass, pressure, temperature data collection.

Figure A7.36 and Figure A7.37 shows the block diagram which contains the graphical source code that defines the functionality of the visual interface.



Figure A7.36. Block diagram which contains the graphical source code that defines the functionality of the user interface (A).



Figure A7.37. Block diagram which contains the graphical source code that defines the functionality of the user interface (B).

Examples of calibration curves used in different experiments



Aluminum analysis using atomic absorption spectroscopy

Figure A7.38. Calibration curve corresponding to total aluminum measurement using atomic absorption spectroscopy.

DOC analysis using 680°C combustion catalytic oxidation - NDIR detection method



Figure A7.39. Calibration curve corresponding to dissolved organic carbon measurement.

Carbohydrate analysis using phenol-sulfuric acid method



Figure A7.40. Calibration curve corresponding to carbohydrates measurement using phenolsulfuric method.

Protein analysis using modified Lowry assay



Figure A7.41. Calibration curve corresponding to proteins measurement using modified Lowry assay.

Ionic composition and ionic strength of Lake Houston water

 Table A7.12.
 Anions and cations composition and ionic strength of Lake Houston water.

lon	Concentration (mg/L)	g/L	z	MW (mg/mmol)	Equivalent weight (mg/meq)	Concentration (meq/L)	C (M)	Cz ²
Al ³⁺	0.120	0.00012	3	26.9815	8.994	0.013	4.45E-06	4.00E-05
Ca ²⁺	18.400	0.01840	2	40.0780	20.039	0.918	4.59E-04	1.84E-03
Fe ³⁺	0.271	0.00027	3	55.8450	18.615	0.015	4.85E-06	4.37E-05
Mg ²⁺	3.160	0.00316	2	24.3050	12.153	0.260	1.30E-04	5.20E-04
Mn ²⁺	0.105	0.00011	2	54.9380	27.469	0.004	1.91E-06	7.64E-06
K⁺	4.400	0.00440	1	39.0983	39.098	0.113	1.13E-04	1.13E-04
Na⁺	35.300	0.03530	1	22.9898	22.990	1.535	1.54E-03	1.54E-03
Total (meq/L)						2.858		
F	0.243	0.00024	1	18.9984	18.998	0.013	1.28E-05	1.28E-05
Cl	33.900	0.03390	1	35.4530	35.453	0.956	9.56E-04	9.56E-04
NO ₂	0.000	0.00000	1	46.0055	46.006	0.000	0.00E+00	0.00E+00
Br⁻	0.049	0.00005	1	79.9040	79.904	0.001	6.13E-07	6.13E-07
NO ₃ ⁻	0.164	0.00016	1	62.0049	62.005	0.003	2.64E-06	2.64E-06
SO4 ²⁻	10.200	0.01020	2	96.0626	48.031	0.212	1.06E-04	4.25E-04
PO4 ³⁻	0.190	0.00019	3	94.9714	31.657	0.006	2.00E-06	1.80E-05
HCO ₃	102.720	0.10272	1	61.0168	61.017	1.683	1.68E-03	1.68E-03
Total (meq/L)						2.874		
						Ionic strength (M)		0.004

Image analysis for particle size and area determination

Particle sizes were analyzed using MATLAB R2009b software where the RGB image was first converted to a 256 grey level image. Enhancement operations including brightness, contrast adjustment and histogram correction were performed on the greyscale image and then histogram-based thresholding was applied to differentiate dark and bright pixels in order to separate the background from the particles/ flocs. The connected components in the resulting binary image were labeled and the inbuilt function regionprops was used to calculate the equivalent diameters of the connected regions. Size distributions were calculated using the equivalent diameter data obtained in terms of pixels and finally converting them to µm.

Following Matlab code was used to find the area and the equivalent diameter in pixels which was later converted to μm .

```
%particle size analysis using microscope images
a = imread('10ppm_matlab.tif');
b = rgb2gray(a);
colormap('gray'), imagesc(b); % all display steps can be commented out
later
    Apply thresholding.
high = logical(b > value);
im = zeros(size(b));
im(high) = 255;
colormap('gray'), imagesc(im);
% Label connected blobs.
L=bwlabel(im);
ids = regionprops(L, 'PixelIdxList','EquivDiameter','Area');
output = zeros(numel(ids), 5, 'double');
```

```
for k = 1:numel(ids)
    output(k,:) = [k max(a(ids(k).PixelIdxList)) ids(k).EquivDiameter
ids(k).Area ids(k).Perimeter];
    max_value(k) = max(a(ids(k).PixelIdxList));
end
% Strip out the values of the area that are 1 (isolated pixels), and
then
% hack the first column to have integer-numbered values again.
test = logical(output(:,4) > 1);
list = output(test,:);
arr = [1:numel(list(:,1))];
list(:,1) = arr;
```

2D fractal dimensions (d_{f,2D}) analysis using ImageJ



Figure A7.42. A screen shot of an example of image based fractal dimension analysis performed using ImageJ software.

Image based-2D fractal dimensions were calculated following the steps given below.

1. Process the image to correct uneven tones and to maximize the contrast between the

floc and the background (adjust contrast, brightness, sharpness, noise

- 2. Subtract the background
- 3. Convert the image to binary format
- Adjust the binary image (e.g., series of erosion and dilation operations) until it closely represents the original floc
- 5. Perform box counting analysis

Fractal dimensions $(d_{f,3D})$ analysis using static light scattering method



Figure A7.43. Light scattering plot obtained for Lake Houston water. The slope represents mass fractal dimension.