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THE EFFECT OF RECYCLED BACKWASH WATER OPERATIONS ON FOULING IN A COAGULATION-ULTRAFILTRATION PROCESS AND IMPACT OF PREOZONATION ON MEMBRANE PRODUCTIVITY

by

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A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the Department of Civil, Environmental, and Construction Engineering
in the College of Engineering and Computer Science
at the University of Central Florida
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ABSTRACT

This dissertation consists of research that focused on pretreatment strategies to reduce fouling of ultrafiltration (UF) membranes used for drinking water treatment, and was segmented into four key components. (1) In the first component of the work, the long-term fouling behavior of a polyethersulfone (PES) hollow-fiber UF membrane was studied at the pilot-scale for treatment of surface water over a one-year period. Pilot testing of a coagulation-flocculation-sedimentation (CFS) pretreatment system revealed that chemically irreversible fouling was poorly correlated with turbidity and total organic carbon. It was also shown that recycled backwash water may have impacted membrane process performance, and that chemically irreversible fouling was responsive to changes in pretreatment configuration. (2) In the second component, pre-oxidation with ozone (preozonation) was then studied as a pretreatment process to reduce natural organic matter (NOM) fouling at the pilot-scale. This work suggested that preozonation reduced long-term chemically irreversible fouling. The chemically reversible fouling index increased by 59%, indicating that preozonation changed the characteristics of the foulants, yielding more effective chemically enhanced backwashes. (3) Bench-scale work that studied changes in NOM characteristics associated with the improved process performance were performed using fluorescent excitation-emission (EEM) spectroscopy and high-performance size-exclusion chromatography (HPSEC). Specifically, ozone was applied prior to a CFS-UF process and compared to a CFS-UF condition without ozone as the control. Although CFS reduced turbidity by 29%, ozone, when integrated with CFS increased turbidity by 58%, impacting downstream UF performance. As expected, ozone, when integrated with CFS and UF reduced filtrate true color by 40%, UV_{254} absorbance by 11%, and SUVA by 30%, relative to the control, indicating that preozonation changed the characteristics of the dissolved organic carbon present in the source water. (4) Follow-up bench-scale research using fluorescent EEM spectroscopy and HPSEC assessed operational strategies that impacted organic fouling. Specifically, the fate of fluorescing substances during the recycling of membrane backwash water (MBWW) ahead of CFS-UF process was investigated. Bench-scale UF membranes were used to generate MBWW from a CFS-treated surface water containing 21 mg/L dissolved organic carbon (DOC) registering a 0.95 cm^{-1} UV_{254} absorbance that had been coagulated with 100 mg/L with polyaluminum chloride. CFS settled water, when processed with UF, produced MBWW containing 9 mg/L DOC registering a 0.25 cm^{-1} UV_{254} absorbance. HPSEC with UV_{254} detection demonstrated an analogous UV_{254} reduction as measured by detector response. However, fluorescence EEM spectroscopy revealed that protein-like substances, known to be associated with irreversible fouling, had been concentrated in the MBWW. In order to evaluate recycling operations on overall DOC removal in a CFS-UF process, a blend of 30% MBWW with 70% of raw water was treated, resulting in an overall DOC removal of 73%. However, without MBWW recycle, the CFS-UF process removed less of the influent DOC (63%). In summary, this research demonstrated that NOM characteristics within MBWW should be considered when recycling backwash water in PES membrane operations, and that preozonation reduces chemically irreversible fouling when incorporated into a CSF-UF system.

This dissertation is dedicated to my parents for their patience and support throughout my entire education.

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Additionally, this work would not have been possible without the support of Harn R/O Systems (Venice, FL). Julie and Jimmie Harn not only collaborated with me on the foundation for my dissertation work, but also offered unwavering support and friendship.

I would also like to express my gratitude to Beth Gentry of the Alameda County Water District (Fremont, CA). Her effort and support of my research were extremely valuable and truly appreciated. Another individual deserving recognition is Dr. Issam Najm of WQTS Inc. (Los Angeles, CA). His assistance and advice were much appreciated.

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LIST OF ABBREVIATIONS

ACWD	Alameda County Water District
AMW	Apparent molecular weight
CEB	Chemically enhanced backwash
CFS	Coagulation, flocculation and sedimentation
CIFI	Chemically irreversible fouling index
CIP	Clean in place
CRFI	Chemically reversible fouling index
DBP	Disinfection by-products
EEM	Excitation-emission matrix
FBRR	Filter Backwash Recycle Rule
FBWW	Filter backwash water
FI	Fouling indices
FRI	Fluorescence Regional Integration
HIFI	Hydraulically irreversible fouling index
HPSEC	High-pressure size exclusion chromatography
HRFI	Hydraulically reversible fouling index
MBWW	Membrane backwash water
MGD	Million gallons per day
MSJWTP	Mission San Jose Surface Water Treatment Plant
MTE	Mass transfer efficiency
NOM	Natural organic matter
PCU	Platinum cobalt color units
PES	Polyethersulfone

SBA	South Bay Aqueduct
SUVA	Specific UV_{254} absorbance
TDS	Total dissolved solids
TFI	Total fouling index
TMP	Transmembrane pressure
TOC	Total organic carbon
TSS	Total suspended solids
UCF	University of Central Florida
UF	Ultrafiltration
UV_{254}	Ultraviolet absorbance at wavelength 254 nm

CHAPTER 1: GENERAL INTRODUCTION

Ultrafiltration in Drinking Water Treatment

The use of ultrafiltration (UF) membranes in drinking water treatment has risen steadily since the early 1990's (Atkinson 2002, Jacangelo et al. 1997). UF membranes are capable of removing microorganisms (including chlorine-resistant protozoa) more efficiently than traditional media filtration. Other advantages of ultrafiltration include effective removal of turbidity, suspended solids, and, with proper pretreatment such as coagulation, virus rejection (Jacangelo et al. 1995, Jacangelo et al. 1989). Therefore, ultrafiltration membranes are often necessary for treatment of surface water and are desirable in areas which experience droughts or have limited groundwater supplies. However, major operational challenges such as control of membrane fouling and the optimization of system recovery still exist for many surface water treatment plants (Gao et al. 2011, Huang et al. 2009). Rising populations in drought prone areas of the Western United States, has further increased the scarcity of potable groundwater sources which has negatively influenced local economic conditions (Giever et al. 2010, Jenkins et al. 2003). As a result, public water systems in the United States are motivated to mitigate membrane fouling while simultaneously reducing their residual streams in a cost-efficient manner. These goals must be met while also continuing to meet existing and emerging regulations. As a result, there exists a need for research which explores issues related to membrane fouling and operational efficiency. Few published studies have examined long-term fouling behavior of membrane systems used in water treatment while also addressing strategies to reduce fouling through operational changes and new pretreatment applications. This dissertation sought to conduct work in each of these areas. Specifically, four concepts were explored in this research: (1) Long-term fouling behavior of ultrafiltration membrane was studied at the pilot-scale revealing that commonly used surrogate measures of water quality did not correlate well with chemically irreversible fouling. (2) Pre-oxidation with ozone was studied as pretreatment to reduce fouling at the pilot-scale. (3) The effect of ozone on organic matter in water was further investigated at the bench-scale. (4) Finally, the impact of recycling of membrane backwash water on system performance was investigated. These four areas were studied through bench-scale and pilot-scale research and are presented in Chapters 2 through 5.

Pre-Oxidation with Ozone

Membrane fouling from natural organic matter (NOM) occurs as organic compounds either deposit and form a cake layer, or adsorb directly to the surface of a membrane (Jermann et al. 2007, Susanto 2007, Zularisam et al. 2006). Fouling is often modeled as resistance-in-series (Boyd and Duranceau 2013, Huang et al. 2008, Nguyen et al. 2011) and can be characterized based on the reversibility of the fouling through cleaning. Organic fouling can lead to decreased permeability and is oftentimes difficult to reverse through cleaning. Therefore, considerable research has been published on pretreatment strategies that remove or destroy organic foulants to reduce the irreversible fraction of fouling.

Previous bench-scale work has identified pre-oxidation with ozone (preozonation) as a treatment strategy to reduce organic fouling of membranes. Ozone is a powerful oxidant that can break down or destroy complex organic compounds known to cause fouling of polymeric membranes (Gao et al. 2011, Van Geluwe et al. 2011). Previous research has generally focused on applications of preozonation with ceramic ozone-resistant membranes (Lee et al. 2013, Lehman and Liu 2009, Sartor et al. 2008). Very few studies have been conducted with polymeric membranes - especially at the pilot-scale. Furthermore, most studies have investigated the use of ozone in direct-filtration applications while other studies, independently, have considered the use of preozonation as a coagulant aid (Bose and Reckhow 2007, Schneider and Tobiason 2000, Singer et al. 2003). However, very few studies have evaluated the integration of ozone, coagulation, and membrane filtration. Specifically, there is a lack of knowledge regarding the downstream impact of ozone-coagulation treatment on membrane fouling. Given that coagulation process are often coupled with UF membranes in surface water treatment, this gap in knowledge is significant. This dissertation research sought to address this gap in knowledge and includes both pilot-scale and bench-scale studies of a preozonation-coagulation-ultrafiltration system with a polyethersulfone membrane.

The Impact of Recycled Backwash Water

Historically, conventional water treatment systems recycle waste streams in order to increase system recovery (Cornwell 2001, Tobiason et al. 2003). For conventional treatment plants with traditional media filters, the most commonly recycled waste is spent filter backwash water (FBWW) (Arora et al. 2001). Previous research has shown that FBWW can contain concentrated levels of the constituents found in raw water including

Cryptosporidium. Public health concerns over the handling of FBWW have led to regulations such as the Filter Backwash Recycle Rule (FBRR) which was implemented in 2001 (Environmental Protection Agency 2002). The FBRR was put in place to protect public health by requiring recycled FBWW to be returned to the head of the treatment process to reduce the risk of accumulating *Cryptosporidium* or other pathogens in a water plant.

Water plants which, in lieu of conventional filters, utilize ultrafiltration membranes instead produce membrane backwash water (MBWW). Most plants choose to recycle a portion of their MBWW in order to improve their system recovery. However, federal regulations that apply specifically to MBWW do not exist. Additionally, only limited research regarding the impacts of recycling of MBWW has been conducted (Boyd et al. 2012, Gora and Walsh 2011, Gottfried et al. 2008). MBWW is concentrated with constituents which were retained by an ultrafiltration membrane and may contain membrane cleaning chemicals. As demonstrated by Boyd et al. (2012), if recycled within a treatment plant, these constituents may impact UF process performance. Given that fouling of UF membranes remains a major challenge for public water systems, there is a need to better understand the impacts of MBWW recycling, the fouling characteristics of these waste streams, and the necessary treatment to mitigate fouling.

Objectives

As conventional water treatment plants around the country continue to replace media filtration systems with ultrafiltration membranes, the need for information regarding fouling control with ozone and the effects of recycling MBWW has become increasingly important. The objectives of the research presented in this dissertation were as follows:

1. Conduct a long-term fouling behavior analysis of a pilot-scale ultrafiltration membrane with a distinction between chemically irreversible and hydraulically irreversible fouling.
2. Determine if the incorporation of preozonation with CFS has an impact on UF process performance at the pilot-scale with a distinction between hydraulically irreversible and chemically irreversible fouling.
3. Investigate the effect of integrating ozone pre-oxidation ahead of CFS as pretreatment to reduce fouling of UF membranes at the bench-scale using organic foulant characterization with fluorescent spectroscopy and high-performance size-exclusion chromatography.
4. At the bench-scale, determine if the incorporation of recycled backwash water has an impact on UF process performance and investigate the fate and characteristics of fluorescing substances during the recycling of membrane backwash water.

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CHAPTER 2: USE OF FOULING INDICES TO DESCRIBE THE LONG-TERM PRODUCTIVITY OF A PILOT-SCALE ULTRAFILTRATION MEMBRANE PROCESS

Abstract

Fouling indices were determined to distinguish and quantify fouling behavior during a long-term pilot test of an ultrafiltration membrane used for surface water treatment. Pilot testing took place over the course of one year and included approximately 5,900 filtration runtime hours. The results demonstrated that hydraulically irreversible fouling experienced during pilot testing increased with runtime as expected. However, chemically irreversible fouling did not consistently increase, but rather was impacted by changes in pretreatment configuration. Process performance was improved when utilizing a pilot-scale clarifier without backwash recycle compared to a full-scale clarifier that included a backwash recycle. Additionally, it was shown that CIFI poorly correlated with feed turbidity, raw water turbidity, and raw water TOC ($R^2 < 0.70$) suggesting that these surrogate measures of water quality were insufficient pretreatment performance indicators. This research also demonstrated the usefulness of fouling indices as an analysis tool for long-term pilot data collected during conventional surface water treatment.

Introduction

Membrane filtration is an established treatment process used in the production of safe drinking water around the world. Ultrafiltration (UF) membrane processes have proven capabilities to reject turbidity and suspended solids. With proper pretreatment such as coagulation-flocculation-sedimentation (CFS), UF membranes are also able to remove viruses, bacteria, and pathogens. The adoption of UF membrane processes for drinking water treatment has increased over the last decade in response to new regulations and the depletion of fresh drinking water supplies due to over mining and drought. However, fouling, which results in a loss of membrane permeability, is considered a barrier to the universal application of membrane processes in the water treatment industry and fouling control is a major focus of water treatment research (Gao et al. 2011). Membrane fouling occurs during filtration as constituents accumulate on or adsorb to the surface of the membrane. Fouling, which results in a loss of membrane permeability (Jacangelo et al. 1989) is often considered the largest barrier to membrane adoption in the water treatment industry.

Typically, full-scale low-pressure membrane processes are operated in a constant flux mode. In this configuration, the transmembrane pressure (TMP) increases during the filtration sequence as a result of fouling. After a set amount of time, the filtration sequence ends and a hydraulic backwash is conducted before the membrane enters the next filtration sequence. The majority of the fouling experienced during a filtration sequence is reversed by this subsequent hydraulic backwash. Permeability loss that persists into the next filtration sequence is referred to as hydraulically irreversible fouling. After several filtration sequences a chemically enhanced backwash (CEB) is executed to restore permeability lost due to hydraulically irreversible fouling. CEBs consist of a chemical soak in combination with a hydraulic backwash. A CEB cycle consists of several filtration sequences culminating in a CEB. Permeability loss across CEB cycles and within a given period of continuous operation at a constant flux, is referred to as chemically irreversible fouling.

There are numerous examples of previous research that emphasizes the importance of distinguishing between the reversible and irreversible components of fouling (Chang et al. 2015, Haberkamp et al. 2011, Jermann et al. 2007, Kimura et al. 2008, Kimura et al. 2014, Nguyen et al. 2011, Peiris et al. 2013, Yamamura et al. 2014). Recently, Boyd and Duranceau (2013) proposed a novel technique for UF process data structuring and analysis referred to as the "TMP balance approach". The TMP balance involves chronologically organizing temperature-corrected TMP data in terms of sequence, cycle, period, and flux case. TMP data is corrected for temperature and is adjusted to account for intrinsic unfouled membrane pressure loss. To identify hydraulically and chemically irreversible fouling, this approach suggests analysis of post-backwash and post-CEB TMP balance data. There has also been considerable work published on fouling indices that are compatible with process data from ultrafiltration systems (Huang et al. 2008, Nguyen et al. 2011). Fouling indices, such as those proposed by Nguyen et al. (2011), are often based on the resistance-in-series model and distinguish between hydraulically irreversible and chemically irreversible fouling. However, the application of fouling indices in published literature, is mostly limited to short term fouling over the course of several days or weeks (Xu and Narbaitz , Zupančič et al. 2014) rather than for long-term fouling trends that span over months of operation. The purpose of this work was to study long-term UF fouling trends using fouling indices during a pilot study for the treatment of a highly fouling surface water.

Background on the Mission San Jose Water Treatment Plant

The pilot study was conducted at the Mission San Jose Water Treatment Plant (MSJWTP) in Fremont, CA. MSJWTP was originally constructed as a conventional surface water treatment plant in 1975 with a capacity of 7.8 million gallons per day (MGD). The original plant used solid-contact clarification and traditional media filtration. In 2007, in anticipation of more stringent water quality regulations, the media filters were replaced with UF polysulfone membranes. The upgraded plant was designed for an average production of 8 MGD with a peak capacity of 10 MGD. Independently, the UF membrane component of the plant was designed to be capable of a maximum capacity of 12.5 MGD with one skid offline in a backwash. This configuration included recycling of membrane backwash water (MBWW) from the ultrafiltration membranes to the head of the plant. This recycle component could represent as much as 10% of the feed flow into the full-scale clarifier. However, the recycle flow was variable depending on the operational conditions of the plant. After blending with the recycle component, the water was dosed with chlorine, ammonia, and ferric chloride coagulant. The free chlorine was required to meet virus log inactivation credit. Ammonia was added to minimize the formation of disinfection by-products. In January of 2008, a report on the operation of the plant retrofit noted that while the UF membranes were able to produce high-quality water and meet regulatory requirements, they were operating at a significantly reduced capacity (3.8 MGD) due to higher than expected rates of fouling and fiber breaks (Sangines and Shaikh 2008). Furthermore, the citric acid used to clean the membranes had originally been upsetting the clarification process due to recycling of the backwash water (Boyd et al. 2012). This issue was subsequently solved by switching to sulfuric acid for backwashing. However, membrane fouling remained a consistent challenge at MSJWTP.

This study represents a pilot-scale demonstration of a polyethersulfone membrane as a replacement to the existing polysulfone ultrafiltration membranes used at MSJWTP. The objective of the work was to study the long-term fouling behavior of the polyethersulfone UF membrane through the application of fouling indices that distinguish between hydraulically irreversible and chemically irreversible fouling.

Materials and Methods

Pilot equipment

The full-scale solid-contact clarification system was not operated year-round. Therefore, to maintain pilot operation, the pretreatment to the pilot UF membrane would at times switch from the full-scale plant clarifier to a pilot-scale solid-contact clarifier. A diagram of the pilot system when treating water from the full-scale clarifier is shown in Figure 2-1, and a diagram of the pilot system when treating water from the pilot-scale clarifier is shown in Figure 2-2.

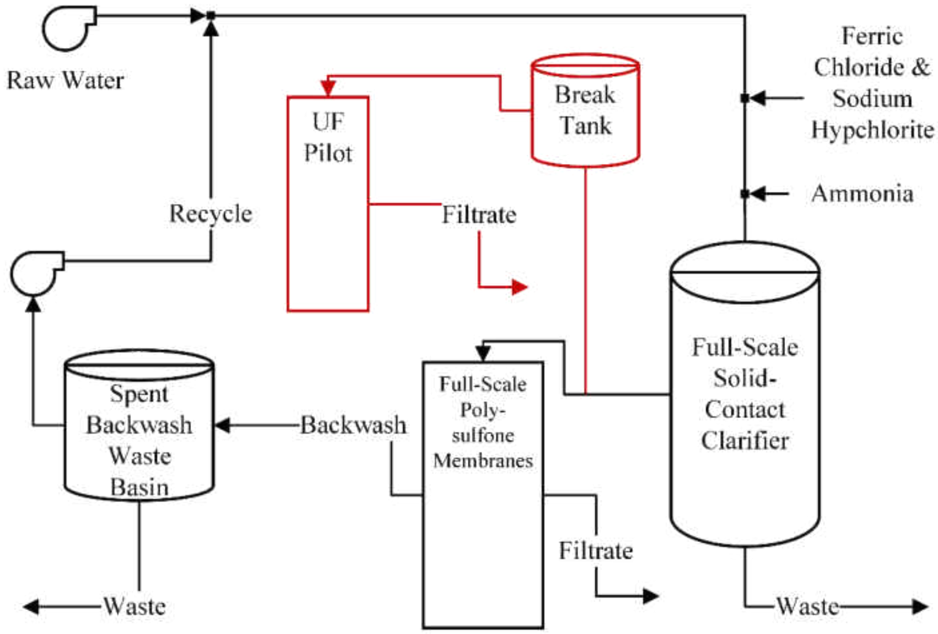

Figure 2-1: Simplified pilot process diagram when utilizing the full-scale clarifier.

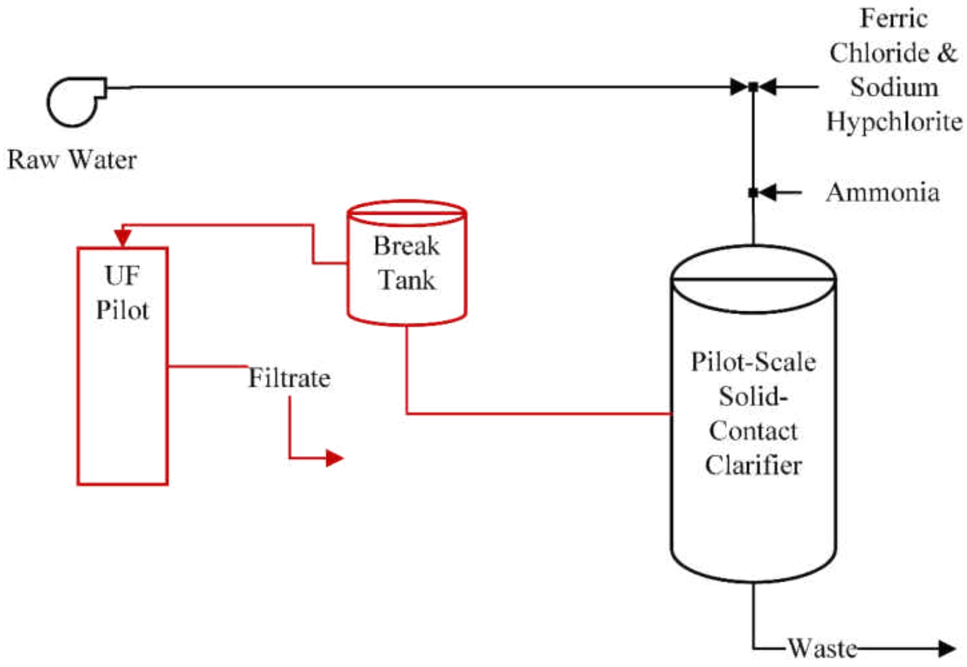

Figure 2-2: Simplified pilot process diagram when utilizing the pilot-scale clarifier.

Ferric chloride was consistently applied at dosages ranging from 25 mg/L to 40 mg/L, for both the full-scale plant clarifier and the pilot clarifier. The clarifier feed water was also dosed with 5 mg/L sodium hypochlorite and ammonia at a 5:1 mass based on free chlorine residual reading prior to the ammonia dosing. The pilot clarifier was a Westech Contact Clarifier Pilot (WesTech Engineering, Inc., Salt Lake City, UT) and operated with a feed flow of 40 gpm.

The ultrafiltration pilot was designed and constructed by Harn R/O Systems, Inc. (Venice, FL) and incorporated a Pentair X-Flow (Enschede, Netherlands) UF module (inside-out, polyethersulfone / polyvinylpyrrolidone membrane). Over the course of the study, the UF pilot was generally operated at a constant filtration flux of 50 gfd. UF pilot process data were logged automatically in two minute increments and included flow rates, filtration flux, transmembrane pressure, temperature, UF feed turbidity, UF filtrate turbidity, and cycle timers. A membrane integrity test was performed manually twice a week.

Three types of cleaning regimes were used for the membrane including hydraulic backwashes, CEBs, and clean-in-places (CIPs). The hydraulic backwashes were conducted every 45 minutes. Each hydraulic backwash was conducted with filtrate water flushed from the outside to the inside of the fibers. Each backwash was conducted at 60 gpm and lasted for 60 seconds. The CEBs were initiated every 24 hours. Each CEB began with a 10-minute soak of 250 mg/L sodium hypochlorite at a pH between 11 and 12. This pH was targeted through the addition of caustic soda. After the chemical soak, the membrane was flushed with filtrate water at 60 gpm for 150 seconds to remove any residual chemical. Then, the

CEB continued with a 10-minute soak with acetic acid and sodium bisulfite (mixed to a pH of 2-3) and then flushed with filtrate water at 60 gpm for 150 seconds to remove chemical residual. CIPs were conducted as needed throughout the pilot study but were not automated.

Source water

The source water during the pilot test came from the South Bay Aqueduct (SBA). The SBA includes water from Sacramento-San Joaquin Delta and/or Lake Del Valle. Blending of these two sources can change seasonally throughout the year. Given the nature of surface water, significant changes in several water quality characteristics are notable throughout a given day. Table 2-1 provides the water quality parameters observed for the raw SBA water during the pilot test. Water quality data were provided by the Alameda County Water District.

Table 2-1: Source Water Variability during pilot testing

Parameter	South Bay Aqueduct		
	Min	Max	Avg.
Alkalinity (mg/Las $CaCO_3$)	50	104	80
Hardness (mg/L as $CaCO_3$)	64	182	97
Total Organic Carbon (mg/L C)	2.5	6.7	4.2
Feed Temperature (°C)	11	27	21

Operational periods

The pilot test included five operational periods, shown in Table 2-2 which took place over the course of one year. Operational periods are defined as segments of at least 200 runtime hours that were not interrupted by CIPs or changes in pretreatment configuration. Period 1 refers to the first stretch of operation from the virgin condition of the UF membrane and lasted approximately 2,500 runtime hours. At this point, the full-scale clarifiers at MSJWTP had to be shut down and the UF pretreatment system was transitioned to the pilot clarifier. Operation under this new configuration represented Period 2. A CIP was not performed during the transition between Period 1 and Period 2. After approximately 1,000 additional runtime hours, the full-scale clarifiers were restarted and the UF pilot pretreatment was changed from the pilot clarifier back to the MSJWTP clarifier. This transition from Period 2 to Period 3 did not include a CIP. At the end of Period 3, the pretreatment was transitioned back to the pilot clarifier, and the UF pilot operated for about 100 runtime hours before a CIP was initiated. This CIP was an extended, overnight CEB soak in acetic acid and sodium bisulfite. Since the period between the pretreatment configuration change and the CIP was less than 200 runtime hours, it was excluded from the analysis.

Table 2-2: UF Pilot Study Period Descriptions

Period	Runtime (hours)	Pretreatment
1	0 - 2513	Full Scale Clarifier
2	2513 - 3498	Pilot-Scale Clarifier
3	3498 - 3787	Full-Scale Clarifier
4	3910 - 5009	Pilot Scale Clarifier
5	5272 - 5932	Full-Scale Clarifier

Therefore, Period 4 began at runtime hour 3,910 and lasted for approximately 1,100 runtime hours before a CIP was performed and the pretreatment was transitioned back to the full-scale clarifier. This CIP consisted of an overnight soak in 2% citric acid. Following the CIP, the first 273 hours of runtime under this new configuration were excluded from the analysis since the pilot underwent a short period of testing at variable flux rates. At runtime 5,272 a constant flux rate was reestablished which marked the beginning of Period 5 which lasted for approximately 700 runtime hours.

Data analysis

Data were collected from the pilot test and grouped by sequence, cycle, and period as described previously (Boyd and Duranceau 2013). The raw two-minute data were collected regardless of the state of the pilot operation. Therefore, data collected near the beginning of a filtration sequence as the pump was ramping up, were often not representative of steady constant flux operation. To remove these data, outliers were detected and removed from raw data by identifying times when the flux set point had not yet been reached.

To quantify and distinguish between hydraulically and chemically irreversible fouling, fouling indices (FI) were determined using the technique described by Nguyen et al. (2011). The fouling index was derived from the resistance-in-series model and can be described as follows:

$$\frac{1}{J_s'} = \frac{\left({}^{J}/_{\Delta P}\right)_0}{\left({}^{J}/_{\Delta P}\right)_V} = 1 + (FI)V \qquad \textbf{(2-1)}$$

Where J is the filtration flux (L h^{-1} m^{-2}), ΔP is the transmembrane pressure (bar) corrected to 20°C, V is the specific permeate volume (L m^{-2}), J'_s is the normalized specific flux (dimensionless) which represents the specific flux for at the clean condition divided by the specific flux after treatment of specific volume V. The FI is the fouling index (m^{-1}) which can be substituted with the total fouling index (TFI), hydraulically irreversible fouling index (HIFI), or the chemically irreversible fouling index (CIFI).

The TFI, HIFI, and CIFI were each determined through linear regression of $1/J'_s$ plotted versus specific volume. Only filtration sequences that contained between 20 and 22 data points were used to determine the TFI indices. For each of these filtration cycles, a linear regression of $1/J'_s$ data against specific volume was conducted and the slope of each regression was taken to be the TFI. Then, the $1/J'_s$ data were averaged for each filtration sequence yielding 45-minute averaged data. These filtration sequence averages were then grouped by CEB cycle. For each CEB cycle (containing at least 20 filtration cycles), a linear regression of the 45-minute averaged filtration sequence $1/J'_s$ data against specific volume was conducted. The HIFI for a given CEB cycle was estimated as the slope of that linear regression. Finally, the $1/J'_s$ data from each CEB cycle was averaged and grouped by study period. For each study period, a linear regression of the averaged CEB cycle $1/J'_s$ data against specific volume was conducted. A linear regression of the average CEB cycle $1/J'_s$ data against specific volume was performed for each period and the slope of each regression was taken to be the CIFI. Average values of the hydraulically reversible fouling index (HRFI) and the chemically reversible fouling index (CRFI) as well as fouling index ratios were also calculated as described by Nguyen et al. (2011).

Results and Discussion

Daily averages of 1/J′s are shown in Figure 2-3. During each study period, the daily averages of 1/J′s generally increased with specific volume treated as expected. However, the magnitude of 1/J′s dropped by approximately 40% immediately after switching to the pilot clarifier following the transition from Period 1 to Period 2.

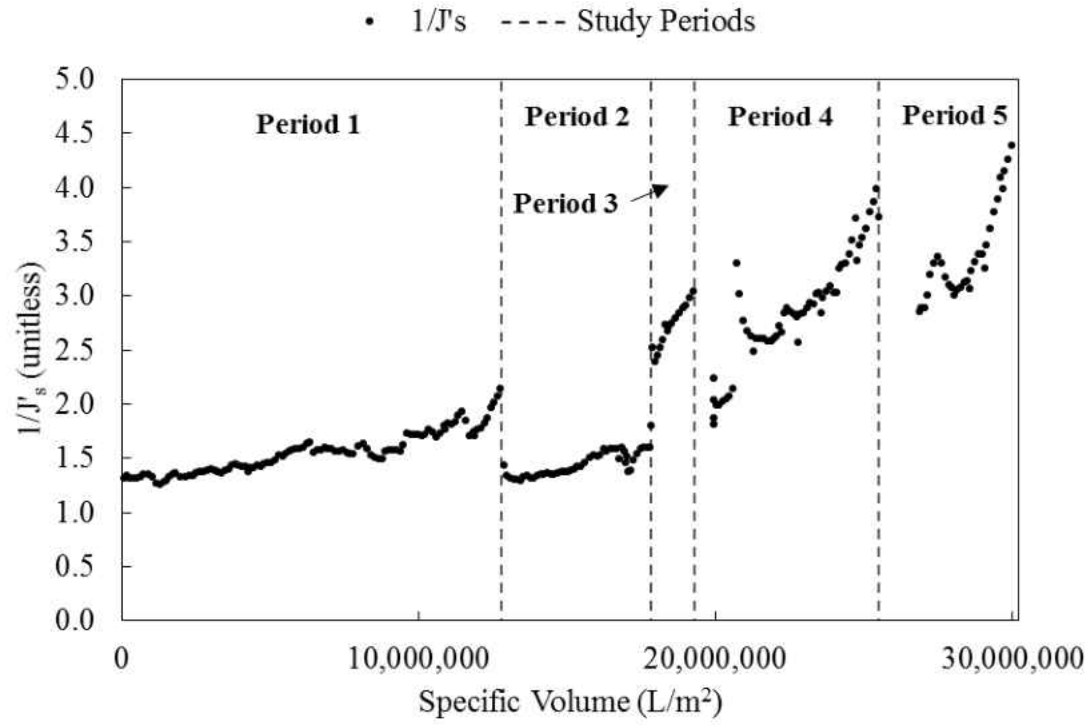

Figure 2-3: Plot of 1/J′s against specific volume for Periods 1-5

This change indicated that a reduction of fouling had taken place. Likewise, a corresponding but opposite affect was observed when transitioning back to the full-scale clarifier in Period 3. The transition to Period 4 again showed an improvement when returning to the pilot clarifier, however this transition involved a CIP so an immediate improvement in performance unrelated to the pretreatment configuration was to be expected. The transition to Period 5 also involved a CIP making an interpretation of the transition more difficult.

The raw water TOC shown in Figure 2-4 indicated that the SBA water TOC increased from Period 1 to Period 2. Therefore, it is likely that the change in pretreatment configuration explained the reduced fouling as opposed to an improvement in source water quality. Furthermore, the UF feed turbidity slightly increased after the transition from Period 1 to Period 2, indicating that the reduction in fouling did not come from an improvement in turbidity removal by the pilot clarifier.

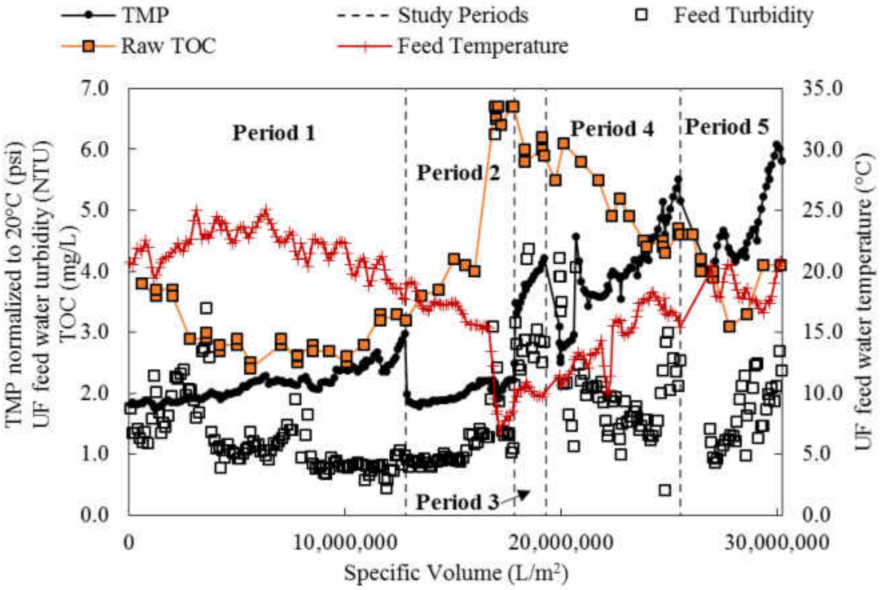

Figure 2-4: Transmembrane pressure, Raw SBA TOC, feed temperature and feed turbidity during study Periods 1-5

The feed turbidity and raw water TOC did increase just before the transition to Period 4, however, the shift in UF pilot performance occurred immediately after the transition to the full-scale clarifier, again indicating that differences in the pretreatment configuration were affecting the UF process performance rather than the performance changing entirely as a function of raw water quality.

These changes in UF performance are reflected in analysis of the TFI as shown in Figure 2-5.

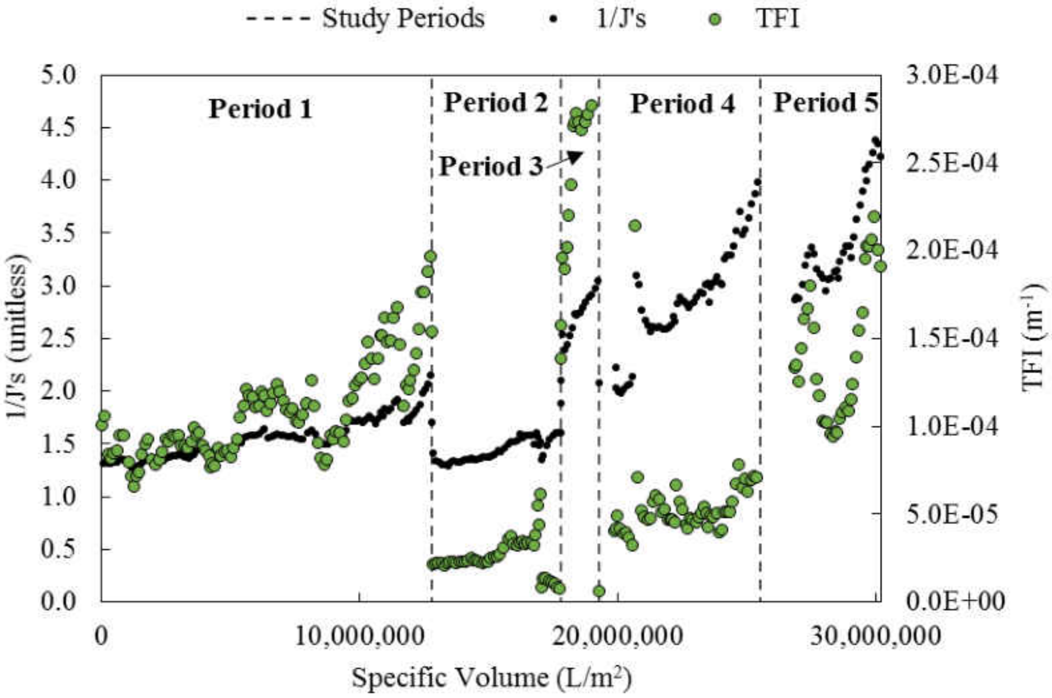

Figure 2-5: Changes in TFI during Periods 1-5

The TFI was higher during Periods 1, 3, and 5 when the UF pilot was operated with the full-scale clarifier compared to Periods 2 and 4 when the UF pilot was operated in conjunction with the pilot clarifier. It is also notable that the TFI was highest during Period 3 suggesting that TFI was not simply impacted as a function of specific volume but rather as a function of the performance of the pretreatment system.

Conversely, the HIFI data shown in Figure 2-6 did not appear to be as impacted by the changes in pretreatment configuration. Rather, the HIFI appeared to gradually increase across periods 1-5 with much less abrupt impacts at the transitions between study periods.

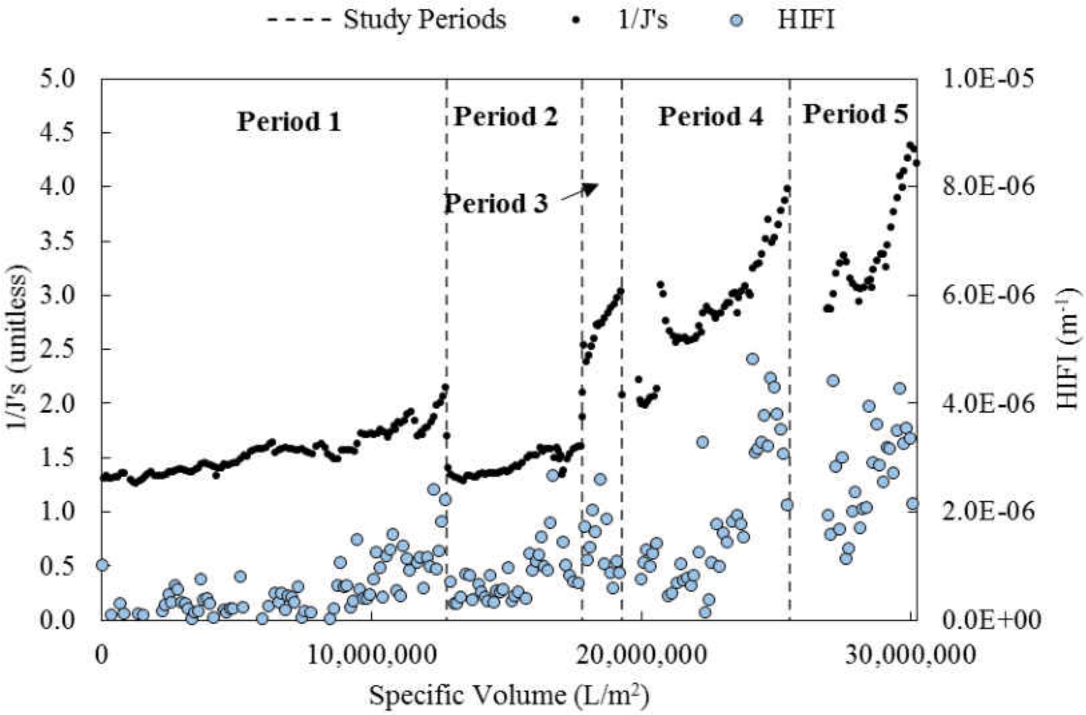

Figure 2-6: Changes in HIFI during Periods 1-5

The CIFI and CRFI for each project period was determined through linear regression and is shown Figure 2-7. The CIFI data reveal that chemically irreversible fouling was the most significant during Period 3. While the CIFI was not significantly changed from Period 1 to Period 2, the CRFI was increased suggesting that the improved TFI in period 2 was due to a larger fraction of chemically reversible fouling which led to overall process performance improvements. Since one of the major differences between the full-scale and pilot-scale clarifier was the incorporation of a recycled backwash stream, it was theorized that the recycled backwash water in the full-scale clarifier may have contributed to chemically irreversible fouling experienced during periods 1, 3, and 5.

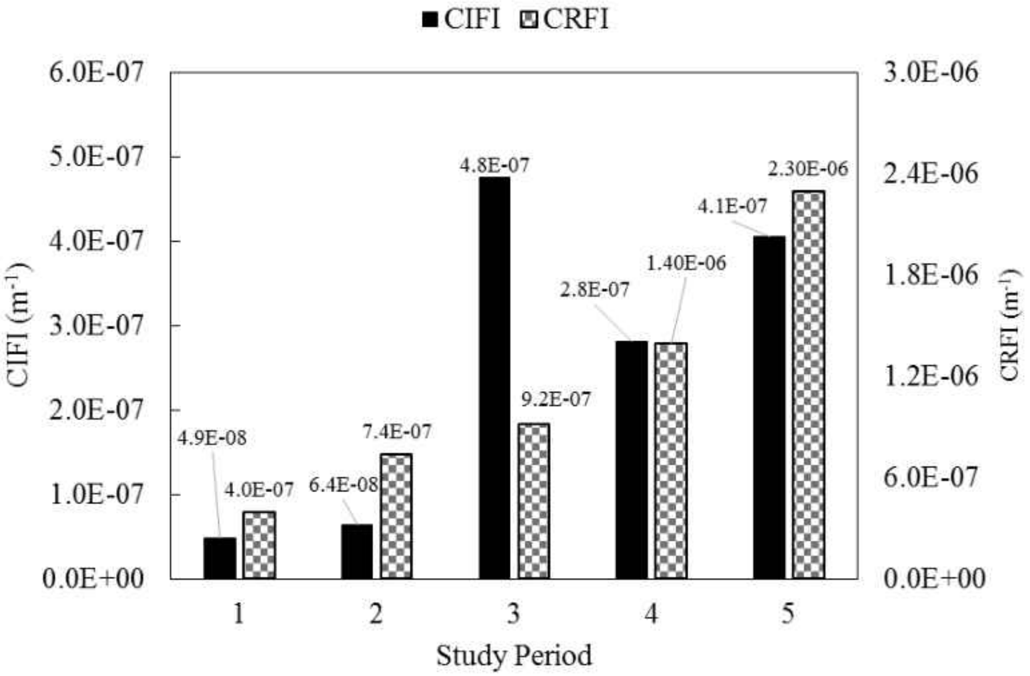

Figure 2-7: Average CIFI and CRFI for each period

The correlation between CIFI and average feed water turbidity, raw water turbidity, and raw water TOC were investigated through linear regression. The results of this analysis are shown in Figure 2-8, Figure 2-9, and Figure 2-10. These figures demonstrate the CIFI was weakly correlated (R^2<0.70) with turbidity and TOC suggesting that CIFI is likely driven by a more specific characteristic component of the organics. This suggestion is in agreement with recent literature (Haberkamp et al. 2011, Peiris et al. 2010, Peiris et al. 2013, Peter-Varbanets et al. 2011).

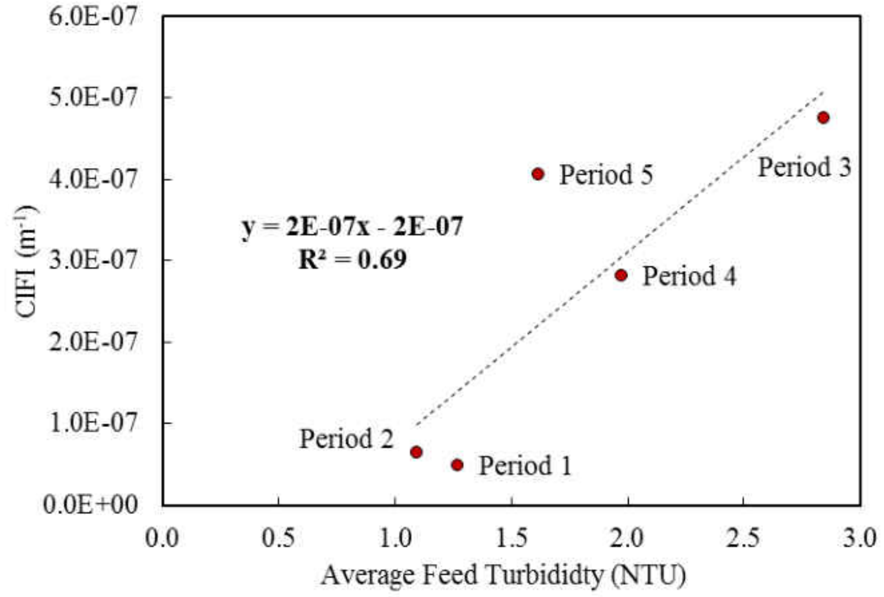

Figure 2-8: Linear regression of CIFI as a function of average feed turbidity

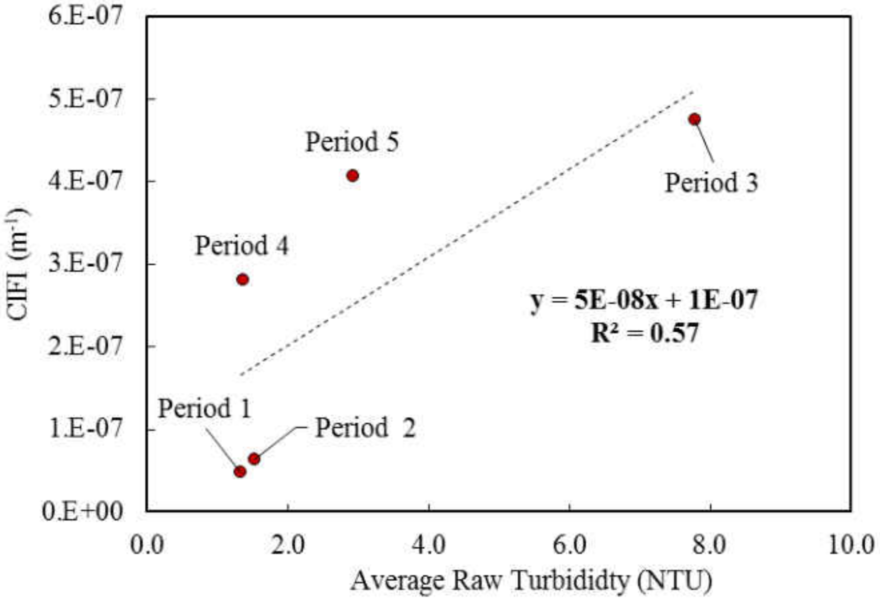

Figure 2-9: Linear regression of CIFI as a function of average raw water turbidity

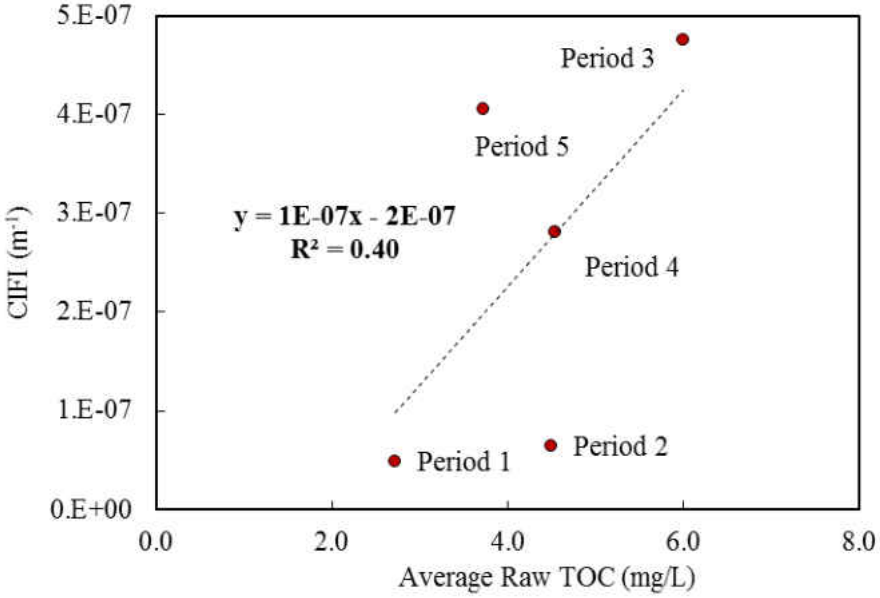

Figure 2-10: Linear regression of CIFI as a function of average raw water TOC

Conclusions

- For Periods 1-5, hydraulically irreversible fouling, as indicated by HIFI increased with runtime and did not appear to be impacted by changes in pretreatment configuration.
- The normalized specific flux of the UF pilot was negatively impacted when the pilot pretreatment configuration switched from the pilot-scale clarifier to the full-scale clarifier.
- Chemically irreversible fouling, as indicated by the CIFI, increased when utilizing the full-scale plant pretreatment system suggesting that recycled backwash water may have an impact on membrane fouling.
- CIFI was poorly correlated with feed turbidity, raw water turbidity, and raw water TOC ($<0.70\ R^2$) suggesting that these surrogate measures of water quality are insufficient to optimize a CFS-UF pretreatment system.
- Future research should further investigate pretreatment strategies that specifically reduce the CIFI.
- Future research should also investigate the factors that led to decreased chemically irreversible fouling experienced during operation of the pilot clarifier such as the effect of recycled membrane backwash water.

Acknowledgments

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CHAPTER 3: ULTRAFILTRATION FOULING REDUCTION WITH THE PILOT-SCALE APPLICATION OF OZONE PRECEDING COAGULATION, FLOCCULATION, AND SEDIMENTATION FOR SURFACE WATER TREATMENT

Abstract

An ultrafiltration (UF) membrane process integrating ozone oxidation prior to a coagulation, flocculation, and sedimentation (CFS) pretreatment configuration processing surface water has been evaluated at the pilot-scale. Unlike prior research limited to short-term bench-scale evaluations, this current study provides information regarding the application of ozone oxidation prior to a CFS-UF pilot process operating over a four-month period (2,800 pilot runtime hours). In this work, changes in the long-term fouling behavior of the UF membrane process in response to the application of ozone prior to CFS pretreatment were characterized using fouling indices. When an average of 2.5 mg/L of ozone was applied prior to coagulation requiring 27 mg/L of polyaluminum chloride and a UF operating water flux of 85 L h^{-1} m^{-2}, the chemically reversible and hydraulically irreversible fouling indices increased by 59% and 40%, respectively. A reduction of chemically irreversible fouling concomitant with a continuous improvement of normalized specific flux was observed over 1,240 pilot runtime hours of ozone application. The total fouling index decreased by 41% as compared to the baseline CFS-UF configuration. This research indicates that the use of ozone oxidation prior to a CFS-UF configuration can reduce membrane fouling when integrated with conventional surface water treatment.

Introduction

Fouling is considered a major challenge faced during the operation of ultrafiltration (UF) membranes for surface water treatment. Pretreatment strategies to mitigate fouling and achieve enhanced removal can include both conventional treatment (coagulation, flocculation and sedimentation, or CFS), and pre-oxidation with ozone (preozonation). Preozonation, when applied under the appropriate conditions, has been shown to reduce downstream membrane fouling (Hashino et al. 2001, Lee et al. 2004, Song et al. 2010), and independently, act as a coagulant aid during conventional treatment (Bose and Reckhow 2007, Sam et al. 2010). However, few studies have investigated the use preozonation with pilot-scale membranes and less work has been published on the integration of both preozonation and CFS pretreatment prior to ultrafiltration.

Bench-scale work has shown that preozonation can remove dissolved organic foulants such as humic substances that are known to cause chemically irreversible membrane fouling (Jones and O'Melia 2001, Jucker and Clark 1994, Peiris et al. 2010). However, since most of this work has considered preozonation application directly ahead of the membrane process, work has been limited to ozone-tolerant ceramic membranes (Karnik et al. 2005, Kim et al. 2008, Lee et al. 2013, Schlichter et al. 2004). Also given the nature of bench-scale work, these studies were primarily short-duration tests.

While these bench-scale studies have provided insight into the possible mechanisms of fouling reduction by preozonation, very few pilot-scale studies have been published to assess the changes in long-term fouling behavior. Hashino et al. (2001) tested an ozone-resistant polyvinylidenefluoride microfiltration membrane for treatment of surface water. In their pilot-scale work, ozone was applied directly ahead of the membrane process so that a residual of 0.3 mg/L O_3 was detectable immediately upstream of the membrane surface. In this configuration, ozone was found to improve membrane permeability. Sartor et al. (2008) evaluated preozonation of surface water prior to ultrafiltration followed by activated carbon filtration. This integrated hybrid process utilized a multi-channel flat sheet ceramic membrane which experienced less overall fouling compared to a control experiment without preozonation. Finally, Lehman and Liu (2009) tested preozonation of wastewater in a pilot study of both ultrafiltration or microfiltration ceramic membranes. They demonstrated that preozonation was effective at removal colloidal natural organic matter found in wastewater which subsequently led to reduced membrane fouling.

These pilot tests have further demonstrated the possible beneficial use of ozone and explored the mechanisms of how preozonation can reduce fouling. However, these studies have either been limited to ceramic membranes or have not considered integrating preozonation with conventional CFS processes. Furthermore, these studies did not quantitatively distinguish between hydraulically irreversible and chemically irreversible fouling. There are numerous examples of previous research that emphasizes the importance of distinguishing between the reversible and irreversible components of fouling (Haberkamp et al. 2011, Jermann et al. 2007, Kimura et al. 2008, Kimura et al. 2014, Nguyen et al. 2011, Peiris et al. 2013, Yamamura et al. 2014). Such a distinction is critical to assessing the long-term impact of incorporating preozonation with a membrane process and to further our understanding of the direct impact of preozonation on membrane foulants. As conventional water treatment plants continue to replace media filtration systems with membranes, the need for such information regarding fouling control using ozone has become increasingly important. Therefore, the purpose of this study was to characterize changes in the fouling behavior of a polymeric UF membrane due to the implementation of preozonation in a CFS-UF process at the pilot scale for treatment of surface water.

Materials and Methods

Pilot study overview

The pilot study was conducted for approximately 4 months in northern California and utilized raw surface water from the South Bay Aqueduct (SBA). A diagram of the complete pilot process is shown in Figure 3-1. The SBA includes water from Sacramento-San Joaquin Delta and, at times, surface water from Lake Del Valle. The average water quality characteristics observed during the pilot study are shown in Table 3-1. Water quality tests were conducted in accordance with standard methods (APHA et al. 2005).

Table 3-1: Average SBA water quality during pilot testing

Parameter	Average
Alkalinity (mg/L)	77
Hardness (mg/L)	94
Turbidity (NTU)	3.3
Total Organic Carbon (mg/L)	6.5
Temperature (°C)	16

The pilot study was conducted in three phases (or periods) to assess the impact of preozonation on membrane fouling behavior in a CFS-UF system. Since this study was one component of a larger pilot project, the initial runtime for Period 1 was 8,645 hours as shown in Table 3-2.

Table 3-2: Description of pilot test periods

Period	Pilot Runtime Hours	Number of Data Points	Process Configuration
1	8645-9626 (981 hrs)	28,774	CFS → UF
2	9626-10238 (612 hrs)	17,621	CFS → UF (with recycle)
3	10238-11477 (1239 hrs)	35,132	Ozone → CFS → UF (with recycle)

Periods 1 and 2 represent a baseline for comparison with Period 3 when preozonation was applied. However, Period 2 is considered independently from Period 1 because during Period 2, a recycle stream was added to the pilot clarifier which returned backwash water from the UF pilot to the head of the treatment system. Table 3-2 also includes the number of data points recorded by the pilot and used during the fouling analysis. A diagram of the complete pilot process used in Period 3 is shown in Figure 3-1.

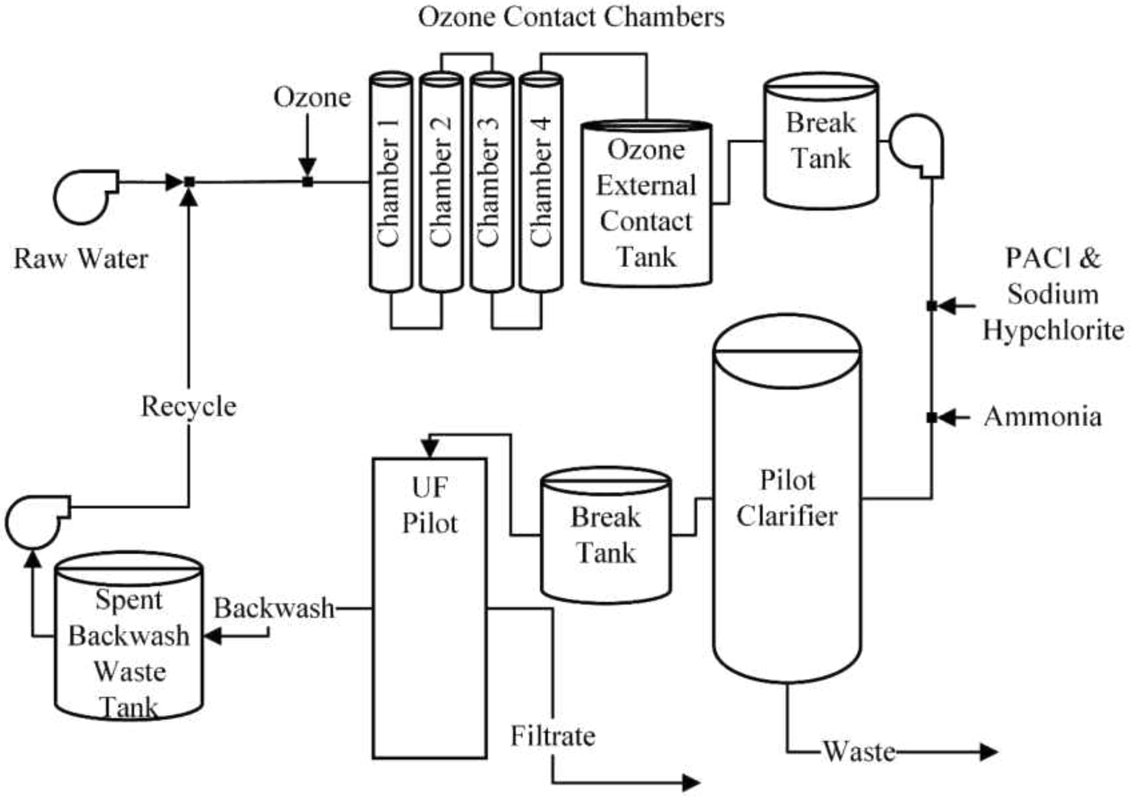

Figure 3-1: Process flow diagram of the complete ozone-CFS-UF pilot system used during Period 3

Pilot-scale preozonation treatment system

The ozone pilot was a Wedeco MiPRO Advanced Oxidation Pilot System (Xylem Water Solutions, Charlotte, NC). The ozone pilot consisted of an ozone generator, controls, oxygen flow meter, oxygen flow control valve, ambient air ozone analyzer, sidestream injection system, four ozone contact chambers, an external ozone contact tank, dissolved ozone analyzer, and an off-gas and vent ozone concentration analyzer. To generate ozone, oxygen was concentrated from ambient air using a pressure swing adsorption system. An ozone generator then converted the concentrated oxygen into ozone. A main control panel was used to vary the oxygen feed rate and power to the ozone generator which in turn adjusted the ozone production rate. Ozone was injected into the raw water stream via an injector and side-stream pump. Contact time was provided by four 37-L vertical stainless steel contact chambers as well as one 1,100-L external vertical contact tank with a 0.9-m diameter. The ozone off-gas concentration from the contact chambers was monitored using an ozone analyzer fed from the top of each contact chamber and top of the external ozone contact tank. After detection, the off-gas from the contact chambers was sent to the ozone destruct unit.

The transferred ozone dose was typically maintained at 2.5 mg/L. However, for a 2-week duration at the start of the test, the dose ranged from 1.8 to 2 mg/L. The dose was also adjusted when conducting calibration of the dissolved ozone analyzer. In this configuration, residual dissolved ozone was not detectable downstream of the final contact chamber during the pilot test.

Pilot-scale solid-contact clarifier

The pilot clarifier was a Westech Contact Clarifier Pilot (WesTech Engineering, Inc., Salt Lake City, UT). The flow through the pilot clarifier was set at 151 liters per minute. The clarifier feed water was dosed with polyaluminum chloride (PACl) between 25 and 30 mg/L to target a maximum turbidity of 2 Nephelometric Turbidity Units (NTU) in the clarifier effluent. The clarifier feed water was also dosed with 5 mg/L sodium hypochlorite and ammonia at a 5:1 mass ratio (chlorine to ammonia ratio) based on free chlorine residual reading prior to the ammonia dosing.

Pilot-scale ultrafiltration membrane

The ultrafiltration pilot was designed and constructed by Harn R/O, Inc. (Venice, FL) and incorporated a Pentair X-Flow (Enschede, Netherlands) UF module. The pilot-scale hollow-fiber UF membrane was composed of a blend of polyethersulfone and polyvinylpyrrolidone and was operated in an inside-out, dead end flow path configuration. The module contained a total of 15,000 fibers which made up a combined of 55 m^2 of total active area. Each fiber had a 0.8 mm diameter and were 1.5 m in total length. The nominal pore size of the membrane was 0.010 µm (0.025 µm absolute) and the molecular weight cut-off was 200,000 Da. Over the course of the study, the UF pilot was operated at a constant filtration flux of 85 $L\ hr^{-1}\ m^{-2}$. UF pilot data were logged automatically in two minute increments and included flow rates, filtration flux, transmembrane pressure (TMP), temperature, UF feed turbidity, UF filtrate turbidity, and cycle timers. Membrane integrity testing was performed manually to assess the membrane for fiber breaks twice a week.

Two cleaning regimes were used for the membrane including hydraulic backwashes with filtrate, and chemically enhanced backwashes (CEBs). The hydraulic backwashes were conducted every 45 minutes. During these backwashes, filtrate was flushed from the outside to the inside of the fibers. Each backwash was conducted at 227 liters per minute and lasted for 60 seconds. The CEBs were initiated every 24 hours. Each CEB began with a 10-minute soak with 250 mg/L sodium hypochlorite that was adjusted to a pH between

11 and 12 using caustic soda, and then was flushed with filtrate water at 227 liters per minute for 150 seconds to remove any chemical residual. Then, the CEB continued with a low-pH 10-minute soak utilizing acetic acid with sodium bisulfite, mixed to a pH of 2-3 and then flushed with filtrate water at 227 liters per minute for 150 seconds to remove chemical residual.

During Periods 2 and 3, backwash waste from both the hydraulic backwashes and the CEBs was collected in a recycle tank. Recycled backwash water was pumped from this tank back to the influent raw water line at a rate of 6.8 liters per minute. This recycle stream achieved a 3% volumetric blend with the incoming raw water.

Analysis of pilot data

To quantify and distinguish between hydraulically and chemically irreversible fouling, data from this pilot test were first organized in terms of filtration sequence, CEB cycle, and study period using the data structure described by Boyd and Duranceau (2013). Fouling indices (FI) were subsequently calculated using the technique described by Nguyen et al. (2011). The fouling index was derived from the resistance-in-series model and can be described as follows:

$$\frac{1}{J'_s} = \frac{\left(J/_{\Delta P}\right)_0}{\left(J/_{\Delta P}\right)_V} = 1 + (FI)V \qquad \textbf{(3-1)}$$

Where J is the filtration flux (L h^{-1} m^{-2}), ΔP is the transmembrane pressure (bar) corrected to 20°C, V is the specific permeate volume (L m^{-2}), J'_s is the normalized specific flux (dimensionless) and FI is the fouling index (m^{-1}) which can be substituted with the total fouling index (TFI), hydraulically irreversible fouling index (HIFI), or the chemically irreversible fouling index (CIFI).

To determine these indices, raw two-minute data were collected regardless of the state of the pilot operation. Therefore, data collected near the beginning of a filtration sequence as the pump was ramping up, were often not representative of steady constant flux operation. To remove these data, outliers were detected and removed from raw data by identifying times when the flux set point had not yet been reached.

Then, the TFI, HIFI, and CIFI were each determined through linear regression of $1/J'_s$ plotted versus specific volume. Only filtration sequences that contained between 20 and 22 data points were used to determine the TFI indices. For each of these filtration cycles, a linear regression of $1/J'_s$ data against specific volume was conducted and the slope of each regression was taken to be the TFI. Then, the $1/J'_s$ data were averaged for each filtration sequence yielding 45-minute averaged data. These filtration sequence averages were then grouped by CEB cycle. For each CEB cycle (containing at least 20 filtration cycles), a linear regression of the 45-minute averaged filtration sequence $1/J'_s$ data against specific volume was conducted. The HIFI for a given CEB cycle was estimated as the slope of that linear regression. Finally, the $1/J'_s$ data from each CEB cycle was averaged and grouped by study period. For each study period, a linear regression of the averaged CEB cycle $1/J'_s$ data against specific volume was conducted. A linear regression of the average CEB cycle $1/J'_s$ data against specific volume was performed for each period and the slope of each regression was taken to be the CIFI. Average values of the hydraulically reversible fouling index (HRFI) and the chemically reversible fouling index (CRFI) as well as fouling index ratios were also calculated as described by Nguyen et al. (2011).

Results and Discussion

Daily averages of $1/J'_s$ are shown in Figure 3-2. During Period 1, the $1/J'_s$ magnitude increased by approximately 30%. Most of this change occurred during the first half of Period 1 as $1/J'_s$ did not rise as rapidly during the second half.

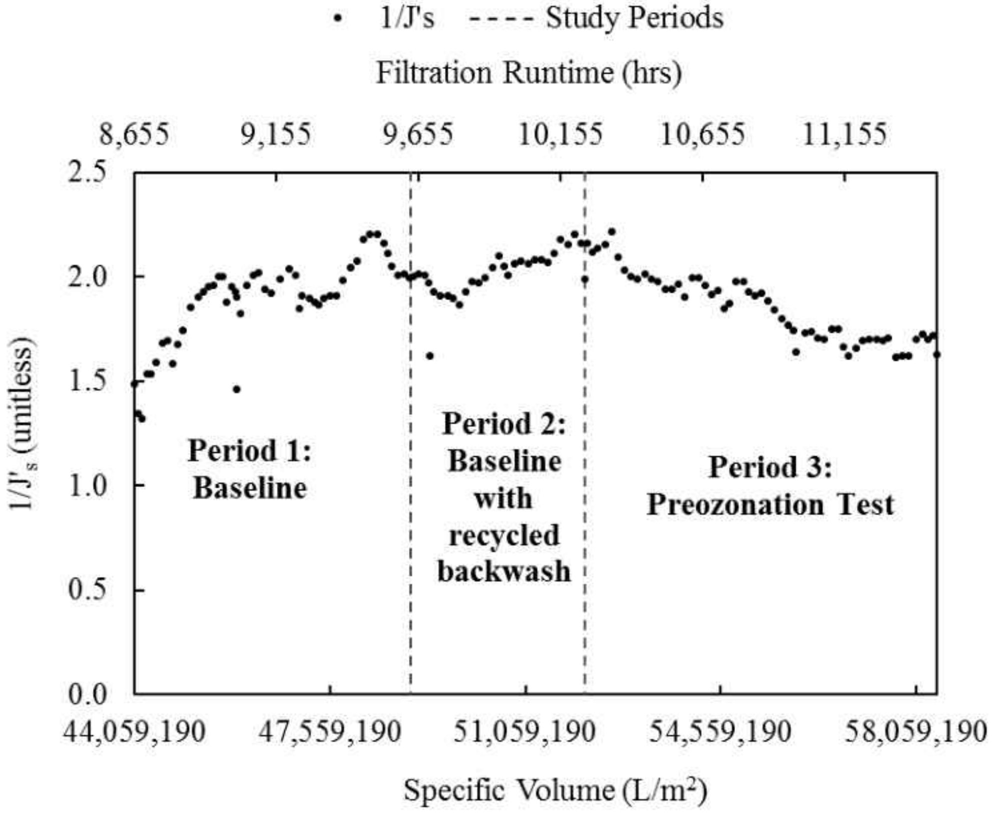

Figure 3-2: Plot of $1/J'_s$ against specific volume for Periods 1-3

In Period 2, the 1/J′s continued to rise and did not seem to be impacted by the implementation of a 3% recycle of ultrafiltration backwash water. However, when preozonation was applied during Period 3, the 1/J′s decreased by approximately 28%.

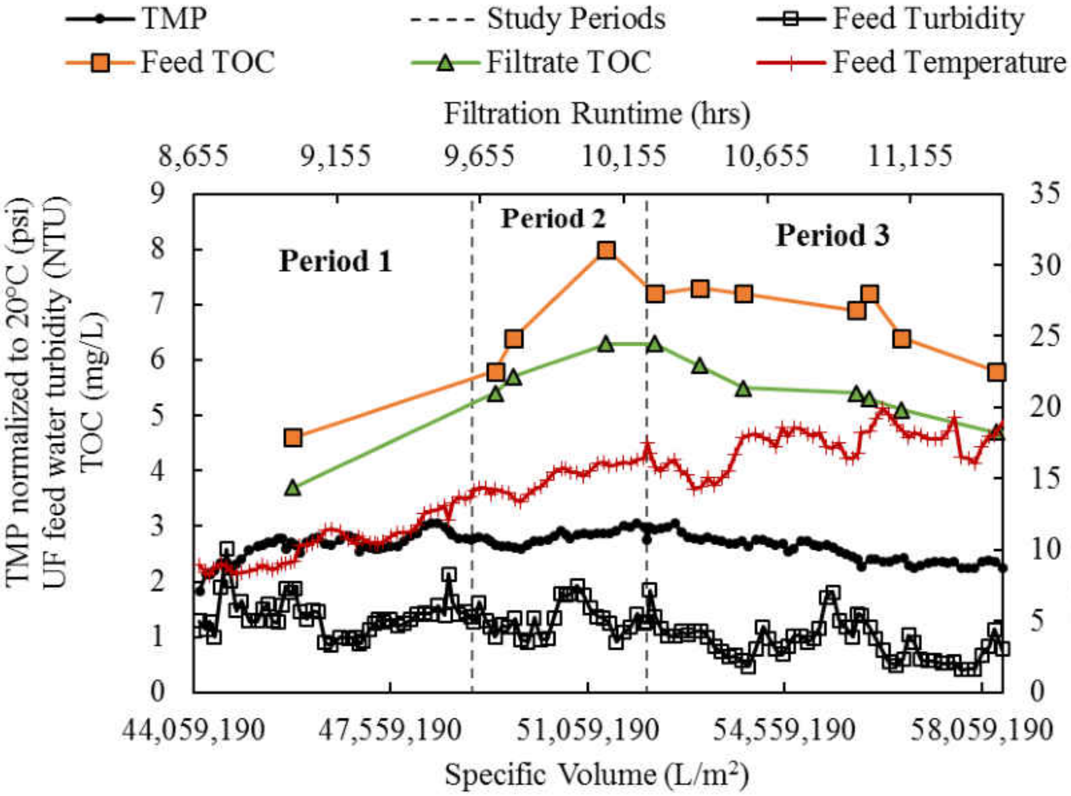

Figure 3-3: Transmembrane pressure, TOC, feed temperature and feed turbidity during study Periods 1-3

Manual integrity testing suggested that no fiber breaks had occurred during the pilot test. This result agreed with total organic carbon (TOC) data displayed in Figure 3-3 which showed no apparent change in the organic carbon removal by the UF pilot during Period 3 as well as Figure 3-4 which showed no indication that filtrate turbidity had been compromised during Period 3.

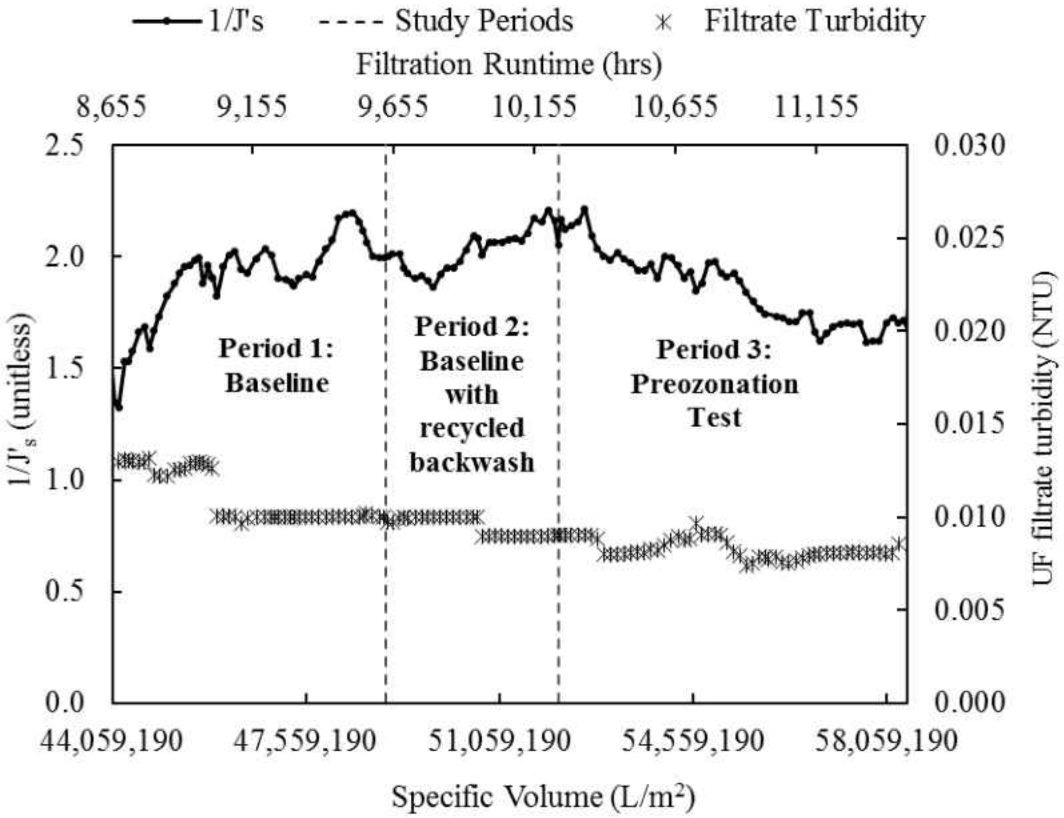

Figure 3-4: Changes in filtrate turbidity during Periods 1-3

To further understand the improvement in permeability during Period 3, the fouling behavior of the ultrafiltration pilot was analyzed by determining the TFI for each filtration cycle during Periods 1 through 3. These TFI values were then averaged by CEB cycle for visual clarity and plotted in Figure 3-5. During Periods 1 and 2 the total fouling index increased as a function of specific volume. When preozonation was applied in Period 3, the TFI began to decrease and by the end of Period 3 the TFI had returned to conditions similar to those during the start of Period 1.

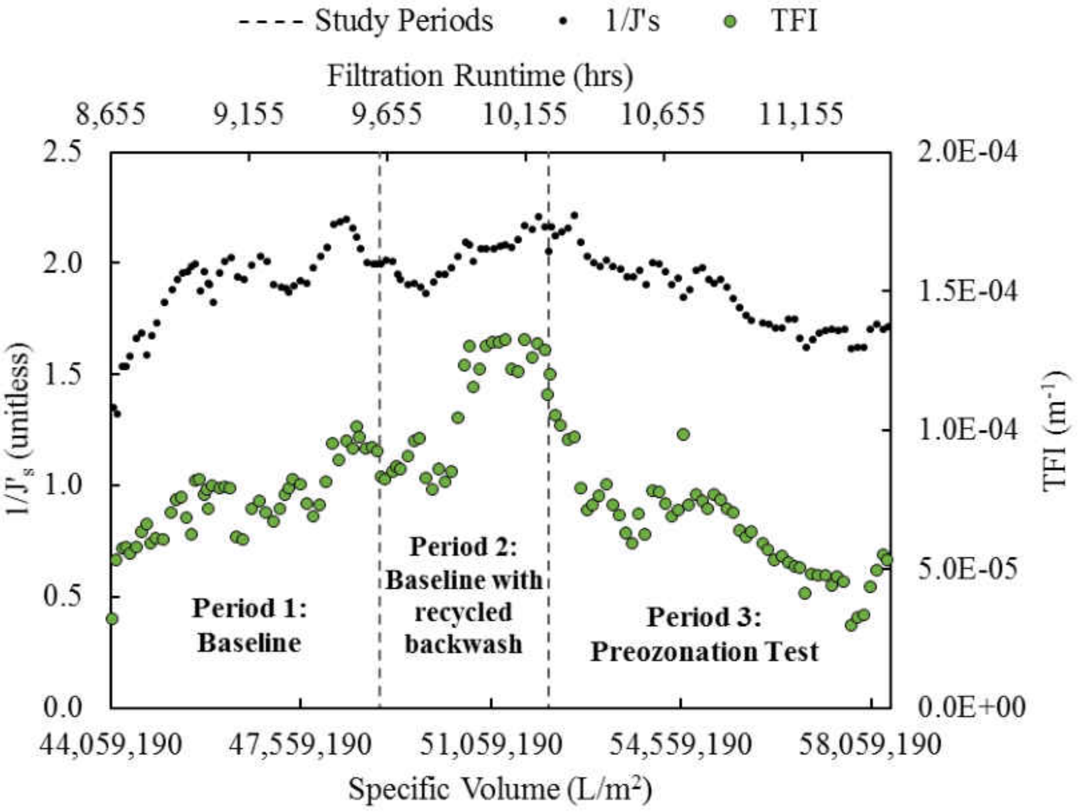

Figure 3-5: Changes in TFI during Periods 1-3

The HIFI data, shown in Figure 3-6, revealed that the hydraulically irreversible fraction of the total fouling was slightly increased during Period 3 and therefore, did not explain the drop in TFI. An overall increase in HIFI had occurred throughout Periods 1-3.

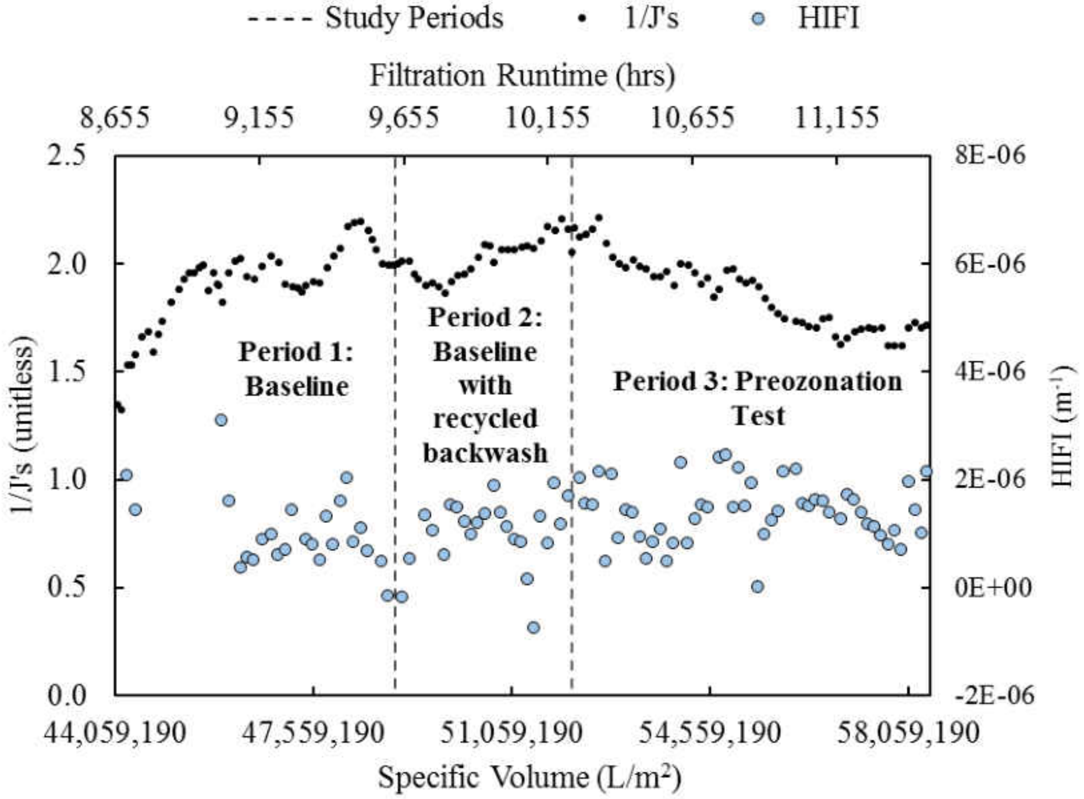

Figure 3-6: Changes in HIFI during Periods 1-3

However, a plot of the HIFI/TFI index ratio shown in Figure 3-7 revealed that the fraction of hydraulically irreversible fouling was higher in Period 3 compared to Periods 1 and 2.

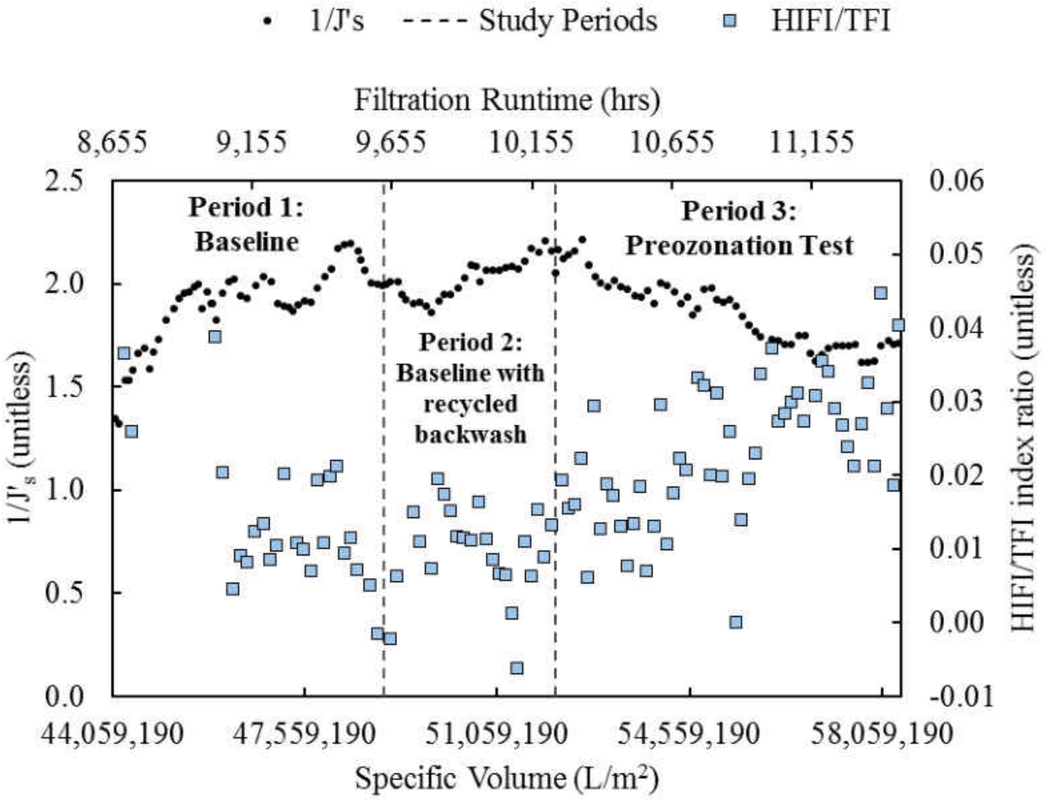

Figure 3-7: Changes in HIFI/TFI ratios during Periods 1-3

The CIFI values for each period were determined and are presented in Figure 3-8. During Period 3, the CIFI was -8.1 x 10^{-6} m^{-1}. The negative CIFI indicated that the membrane was experiencing a long-term “cleaning” trend whereby the CEBs were effectively restoring the membrane to increased permeability day-over-day.

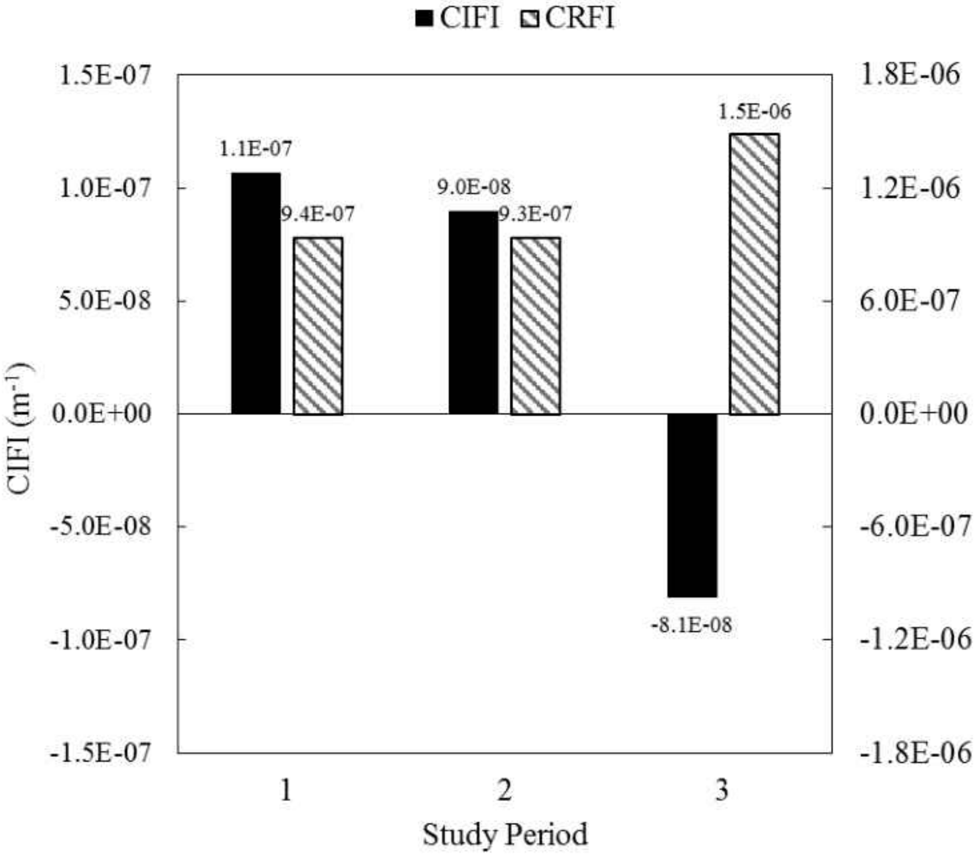

Figure 3-8: Average CIFI for each period

Likewise, the CRFI was 1.5 x 10^{-6} m^{-1} which represented a 59% increase in the chemical reversibility of the fouling experienced in Period 3 compared to Periods 1 and 2. This result suggested that the implementation of preozonation with CFS pretreatment had changed the characteristics of the foulants such that the fouling was now more chemically reversible than during Periods 1 and 2. Likewise, a plot of the CIFI/HIFI index ratio (Figure 3-9) showed that the fraction of chemically irreversible fouling was lower in Period 3 compared to Periods 1 and 2.

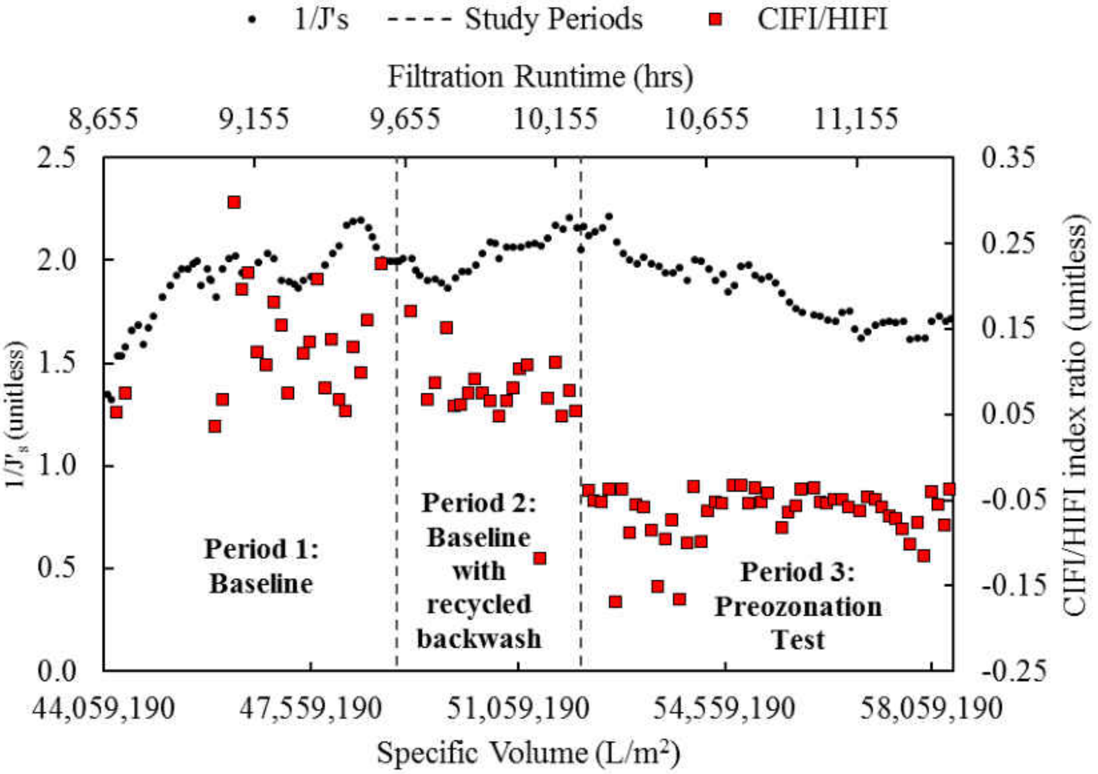

Figure 3-9: Changes in CIFI/HIFI ratios during Periods 1-3

Average fouling indices from Periods 1-3 are compared in Figure 3-10. These results further indicated that preozonation changed the characteristics of the foulants such that the chemically enhanced backwashes became significantly improved. However, hydraulically irreversible fouling was higher during Period 3.

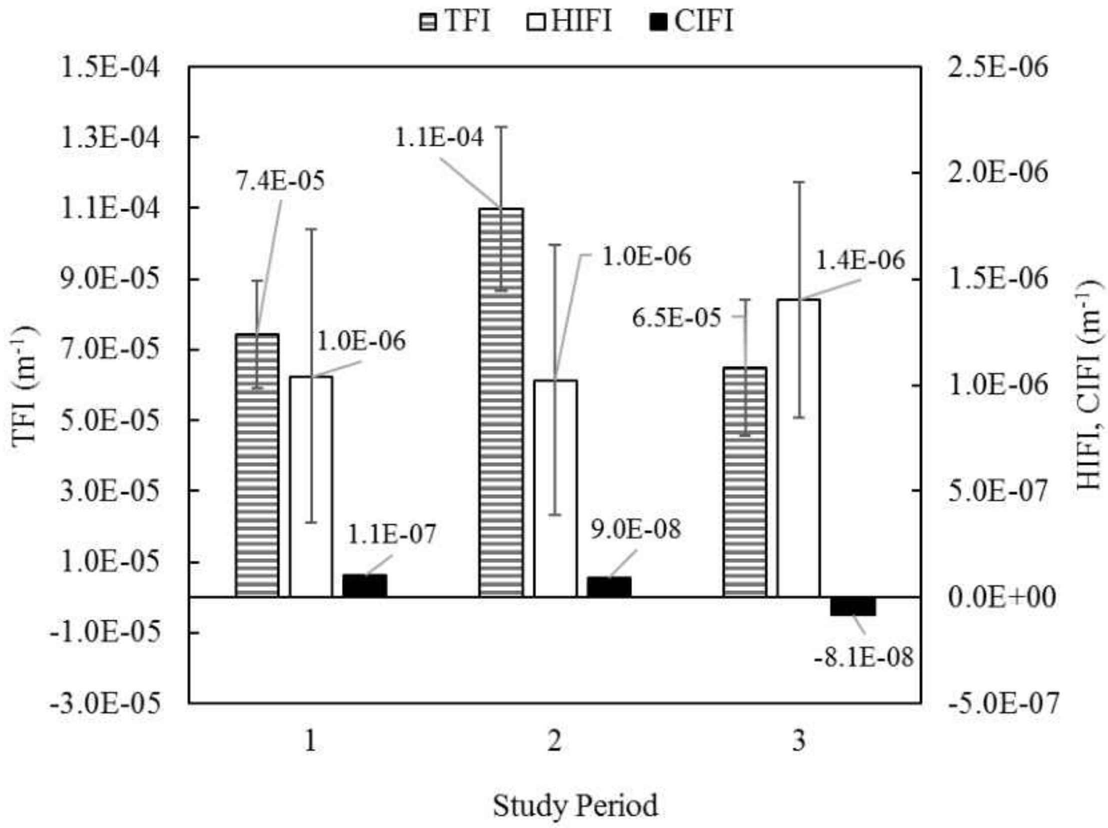

Figure 3-10: Comparison of average TFI, HIFI, and CIFI for each period with error bars representing one standard deviation

These data suggest that the UF process could have been further optimized by increasing the frequency of chemically enhanced backwashes when applying preozonation. Additional organic matter characterization may also aid optimization of the membrane process as this data may reveal the underlying changes to the organic foulants by ozonation which led to the improved chemical reversibility of the foulants.

Conclusions

The goal of this work was to investigate the effect of preozonation on the fouling behavior of an ultrafiltration membrane used to treat coagulated surface water at the pilot-scale. The major findings of this study are as follows:

- Fouling indices revealed that membrane cleaning performance was affected by the implementation of preozonation.
- TFI was reduced by 41% when preozonation was applied suggesting that the overall fouling rate had been reduced.
- Preozonation led to improved chemically enhanced backwashes which increased CRFI by 59% and effectively eliminated chemically irreversible fouling.
- Hydraulically irreversible fouling was increased when preozonation was applied as indicated by HIFI.

Acknowledgments

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CHAPTER 4: PREOZONATION EFFECTS ON ORGANIC FOULING IN A COAGULATION-ULTRAFILTRATION MEMBRANE PROCESS

Abstract

The effect of integrating ozone ahead of coagulation, flocculation and sedimentation (CFS) as pretreatment to reduce organic fouling of ultrafiltration (UF) membranes has been investigated at the bench-scale for treatment of surface water. Ozone was applied prior to a CFS-UF process and compared to a CFS-UF condition without ozone as the control. Although CFS alone reduced turbidity by 29%, ozone, when integrated with CFS increased turbidity by 63%. However, ozone, when integrated with CFS and UF reduced filtrate true color by 38%, UV_{254} absorbance by 10%, and SUVA by 28%, relative to the control, indicating that while ozone had impaired the removal of turbidity during CFS pretreatment, it had improved the removal of aromatic-rich organic foulants. Fluorescent excitation-emission matrices confirmed that humic acid-like and fulvic acid-like substances known to cause irreversible fouling were retained on the control membrane, but were absent on the membrane when integrating ozone with CFS pretreatment.

Introduction

Membrane filtration is an important and widely used process in the production of safe drinking water. Ultrafiltration (UF) is a low-pressure membrane process that is used primarily to remove turbidity and suspended solids. With pretreatment, such as coagulation, UF membranes can also be used for removal of viruses, bacteria, and pathogens. Furukawa (2008) reported that research, coupled with advancements in membrane technology and increasingly stringent regulations, have led to further adoption of low-pressure membranes for treatment of surface water. In many cases, adoption of membrane technology has come in the form of retrofits to existing conventional surface water treatment plants, whereby traditional granular media filters are replaced with UF membranes. However, a major challenge associated with membrane filtration is fouling. Fouling of membranes results in a loss of permeability and an increase in the energy required to filter water (Jacangelo et al. 1989). Effective operation of ultrafiltration (UF) membranes for surface water treatment often requires management of membrane fouling and optimization of conventional pretreatment processes for fouling minimization. In particular, organic fouling is often mitigated through the use of a variety of pretreatment processes. As a result, extensive research on pretreatment processes such as coagulation (Kimura et al. 2014), biofiltration (Netcher et al. 2016), and pre-oxidation with ozone (Van Geluwe et al. 2011) continue to be of vital importance. Few studies have attempted to investigate how various pretreatment processes can be integrated with each other to minimize membrane fouling. In a review of ultrafiltration fouling control, Gao et al. (2011) only identified a single study that included integrated pretreatment, namely an ozone-adsorption-coagulation pretreatment system. In this work, the integration of adsorption following ozonation resulted in an adverse impact on membrane fouling (Mozia et al. 2006). Alternatively, the integration of ozone and coagulation pretreatment prior to ultrafiltration has not been evaluated extensively in the literature. Pre-oxidation with ozone (preozonation) has been shown to reduce membrane fouling, and independently, to act as a coagulant aid during conventional treatment under certain conditions (Bose et al. 2007, Sam et al. 2010). However, there is a gap in knowledge regarding how preozonation can be utilized for reduction of organic fouling of membranes when used in conjunction with conventional surface water treatment coagulation processes.

Ozone has historically been applied in water treatment for a variety of purposes (Camel et al. 1998). Ozone is a strong oxidant and can therefore assist in treatment of iron, manganese, color, taste, and odor. Ozone can also be used as a disinfectant for inactivation of chlorine-resistant protozoa (von Gunten 2003). Chlorinated disinfection by-product formation potential can be reduced by substituting chlorine with ozone for disinfection (Camel & Bermond 1998, Farahbakhsh et al. 2004). Several researchers have also demonstrated that ozone can also be used as a coagulant aid (Camel & Bermond 1998, Jekel 1998, Schneider et al. 2000, Bose & Reckhow 2007). This is typically accomplished by pre-oxidizing water with ozone prior to coagulation. However, ozone can also be applied at an intermediate stage as demonstrated by Bose and Reckhow (2007). The results of these studies have revealed that preozonation can enhance or have an adverse effect on the coagulation process depending on various conditions that include pH, alkalinity, hardness, and natural organic matter (NOM) content. However, the fundamental mechanisms dictating the optimal conditions for use of ozone as a coagulant aid are not entirely clear. Also of note, the vast majority of these studies have been conducted under the assumption that coagulation would be followed by traditional media filtration, or were focused primarily on NOM removal by coagulation and did not make mention of the filtration technique.

Preozonation has also been proposed as a pretreatment to directly reduce organic fouling of membranes (Van Geluwe Braeken & Van der Bruggen 2011, Orta de Velásquez et al. 2013, Barry et al. 2014, Moslemi et al. 2014, Szymanska et al. 2014, Fujioka et al. 2015). The use of ozone for this purpose has been studied because ozone is known to destroy the aromatic-rich and humic-like NOM which are associated with irreversible organic fouling of ultrafiltration membranes (Jucker et al. 1994, Jones et al. 2001, Peiris et al. 2010). However, most studies have only considered using ozone directly ahead of the membrane with no intermediate processes. Previous work has also been largely limited to fouling of ceramic membranes since ozone resistant polymeric membranes were not available (Lee et al. 2004). Park (2002) studied preozonation to reduce fouling of polyvinylidene difluoride membrane. This work demonstrated that preozonation could improve permeate flux by 10% but could not eliminate fouling entirely. Schlichter et al. (2003) suggested that the increase in flux from ozone was due to the impact of ozone on the organic foulants by demonstrating that preozonation of distilled water had no effect on the permeate flux for a ceramic membrane. When conducting trials with humic acid, a reduction in fouling was observed along with an increase in permeate flux. Lee Jang and Watanabe (2004) studied the mechanism by which ozone was reducing fouling. Namely, they observed that humic substances were being broken down to lower molecular weight organic compounds which were passing through the membrane and leading to elevated organic matter in the permeate water. Schlichter et al. (2004) found similar results but included activated carbon filtration downstream of the membrane process which reduced the organic matter in the treated water.

While these studies have investigated the use of ozone to directly reduce organic fouling of membranes and other studies, independently, have considered the use of preozonation as a coagulant aid, very few studies have evaluated the integration of ozone, coagulation, and membrane filtration. Specifically, there is a lack of knowledge regarding the downstream impact of ozone-coagulation treatment on organic matter known to cause irreversible membrane fouling. As conventional water treatment plants continue to replace media filtration systems with membranes, the need for such information regarding fouling control with ozone has become increasingly important. The aim of this bench-scale research was to take the first steps in evaluating the integration of preozonation with coagulation and ultrafiltration. Specifically, the quantity and characteristics of organic foulants were tracked in a bench-scale evaluation that compared integrated conventional pretreatment both with and without ozone. Organic characterization was achieved through the application of fluorescence spectroscopy, ultraviolet absorbance, and size-exclusion chromatography in order to track the aromatic-rich components of the NOM known to cause chemically irreversible fouling of polymeric membranes.

Materials and Methods

Bench-Scale Testing

Raw surface water was collected from the Lake Manatee Water Treatment Plant in Manatee County, Florida. This source water, which contains approximately 20 mg/L dissolved organic carbon (DOC), was chosen because it is currently treated through conventional surface water treatment with media filtration but is slated to transition to ultrafiltration membranes (Sethi et al. 2015). Lake Manatee raw surface water was subsequently treated under two scenarios: one with preozonation, and a control study without preozonation.

Preozonation

For the evaluation with preozonation, an applied ozone dose of approximately 14 mg/L was achieved using the bench-scale ozone generator at Guardian Manufacturing's Research & Development Lab (2750 Dillard Road, Suite 12, Eustis, Florida 32726). The transferred ozone dose was chosen to provide approximately 0.7 mg O_3/mg DOC which was recommended for optimal coagulation performance in previous research by Schneider and Tobiason (2000). Raw surface water was dosed in batches of 20 L at a time. Ozone residual was not detectable after dosing the surface water. Figure 4-1 illustrates an application of ozone to one of the batches of surface water. The target dose of 14 mg/L was achieved after approximately 800 seconds. The mass transfer efficiency (MTE) of the ozone dose had leveled off at approximately 35% after 7 minutes.

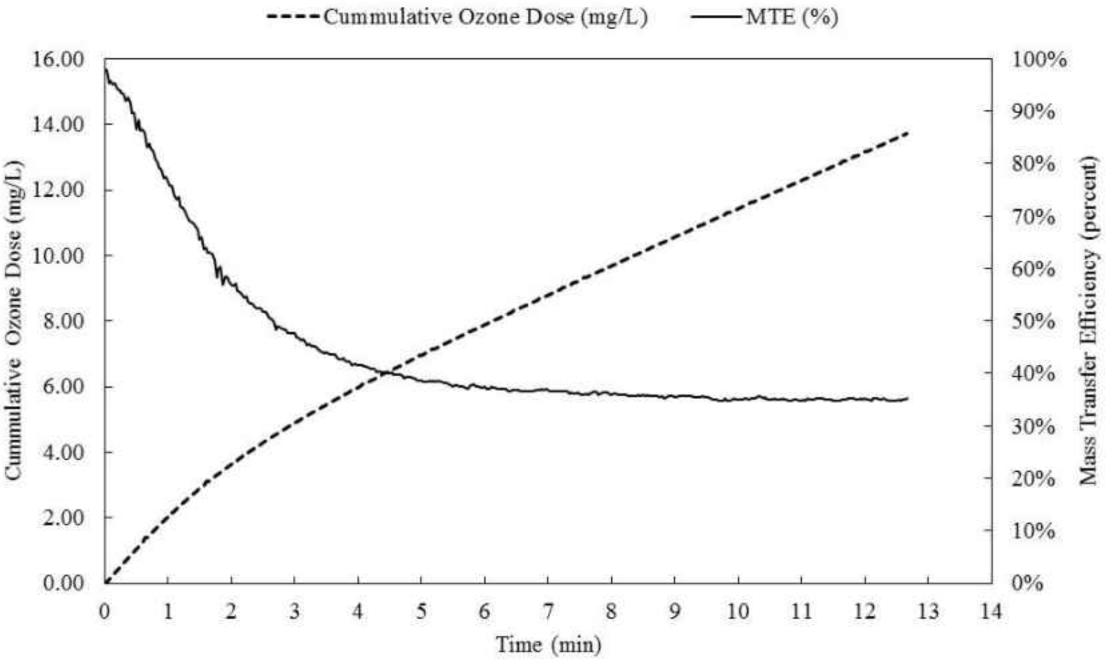

Figure 4-1: Transferred Ozone Dose Curve

Bench-Scale Jar Testing

Bench-scale jar testing was used to simulate coagulation-flocculation-sedimentation (CFS). A jar testing apparatus (Phipps and Bird, Richmond, VA) was used to conduct the test. Six jars were filled with two liters of either surface water, or ozonated surface water. Each jar was dosed with approximately 100 mg/L of polyaluminum chloride (PACl) coagulant. This dose was chosen based on information provided by the Lake Manatee Water Treatment Plant. The jar testing sequence was chosen to match the conditions of a surface water treatment plant that utilizes a solid-contact clarifier. This sequence consisted of 11 seconds at 300 rpm to simulate a rapid mix, 4 minutes and 14 seconds at 100 rpm to simulate mixing at the inlet works, 8 minutes at 60 rpm to simulate the clarifier mixing zone, 7 minutes at 5 rpm to simulate the clarifier flocculation zone, and 10 minutes at 0 rpm to simulate settling. Water quality samples of the supernatant from each jar was collected independently. The jar testing and water quality testing was conducted in duplicate. The supernatant from the jar test was then transferred to the feed tank of the bench-scale membrane apparatus.

Bench-Scale Ultrafiltration Testing

Bench-scale hollow-fiber UF membranes that were composed of a blend of polyethersulfone and polyvinylpyrrolidone were used in the experiments. The membrane element was designed to be operated with an inside-out, dead-end flow path. Each module contained a total of 120 fibers which made up a combined of 0.08 m^2 of total active area. Each fiber had a 0.8 mm diameter and were 300 mm in length. The nominal pore size of the membrane was 0.010 µm (absolute, 0.025 µm) and the molecular weight cut-off was 200,000 Da. The filtration experiments were carried out by pumping feed water to a mini-module using a peristaltic pump. A permeate flux of 85 L/m-hr was maintained. Hydraulic backwashing at 255 L/m-hr for 60 seconds was conducted after approximately 45 minutes of filtration. Samples were collected in duplicate throughout each filtration cycle.

Analytical Methods

Each sample collected during the bench-scale experiments were tested for water quality parameters including pH, turbidity, temperature, and conductivity in accordance with standard methods (APHA et al. 2005). Additional parameters which relate to organic characterization were measured including DOC, UV-Vis spectra, true color, and fluorescence excitation-emission spectra.

DOC was determined by first filtering samples with a pre-washed 0.45 µm membrane filter followed by analysis using a Fusion Total Organic Carbon Analyzer (Teledyne Tekmar Inc, Mason, OH) according to Standard Method 5310C (APHA AWWA & WEF 2005). UV-Vis spectra were collected using a DR5000 spectrophotometer (Hach, Loveland, CO). Samples were first filtered through a pre-washed 0.45 µm membrane filter before undergoing UV-Vis scans. Each scan was conducted from wavelength 200 nm to 600 nm in 1-nm intervals.

Fluorescence excitation-emission spectroscopy was conducted to further characterize the dissolved organic matter. Prior to fluorescence analysis, samples were filtered with a 0.45 µm membrane filter to remove particulates. Without further pretreatment, fluorescence excitation-emission matrix (EEM) spectra were collected using a Shimadzu RF-6000 spectrofluorophotometer (Kyoto, Japan). The emission intensity readings were captured in 1-nm wavelength intervals between 280 nm and 600 nm for excitation wavelengths ranging from 200 nm to 400 nm in 5-nm intervals. The excitation and emission slits were set to a 10-nm band-pass. The Raleigh scattering effect was minimized by subtracting the fluorescence spectra collected from a blank sample of deionized water. Given that the organic content of the surface water was thought to potentially contain more than 20 mg/L for some samples, it was also important to account for the absorption of light by the DOC of the sample (commonly referred to as the inner filter effect). A correction for the inner filter effect was applied to the blank-subtracted spectra following the method described by Westerhoff et al. (2001). Fluorescence Regional Integration (FRI) was used to quantify and interpret the results of each EEM sample taken (Chen et al. 2003). FRI involves dividing an EEM into characteristic regions that represent different types of organic matter as shown in Table 4-1. A normalized, integrated volume ($\phi_{i,n}$) was determined for the peaks in each region for quantitative comparison. A legend of the regions is shown in Figure 4-2.

Table 4-1: Description of FRI regions

EEM Region	Excitation Range	Emission Range	Description
Region I	200 – 250	280 – 330	Aromatic Protein-Like
Region II	200 – 250	330 – 380	Aromatic Protein-Like
Region III	200 – 250	380 – 600	Fulvic Acid-Like
Region IV	250 – 340	280 – 380	Soluble Microbial By-Product-Like
Region V	250 – 400	380 – 600	Humic Acid-Like

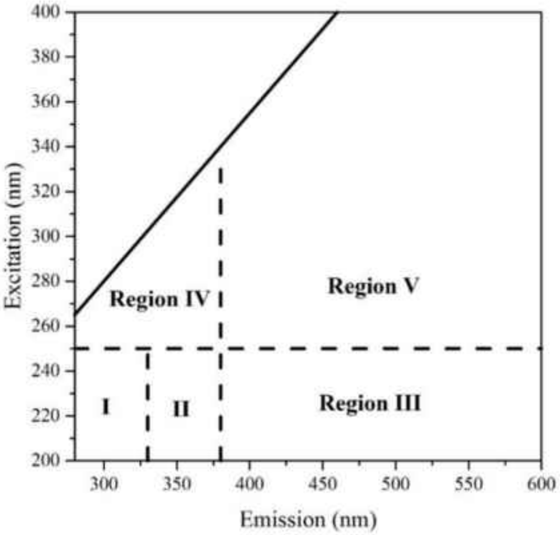

Figure 4-2: Fluorescence Regional Integration legend

The apparent molecular weight distribution (AMW) of the natural organic matter was determined using high-performance size exclusion chromatography (HPSEC). Established HPSEC methodology were followed and are provided in detail elsewhere (Chin et al. 1994, Zhou et al. 2000). Briefly, a Perkin Elmer Series 200 HPLC system consisting of a pump and autosampler were used. The mobile phase was a phosphate buffer that consisted of 2mM K_2HPO_4, 2mM KH_2PO_4, and 0.1 M NaCl. The mobile phase was pumped at a 1mL/min flow rate. The sample injection volume was 150 µL. The size exclusion column used was a Protein-Pak 125 (Waters Inc, Milford, MA). Calibration was achieved with molecular weight standards prepared from HPLC-grade acetone, salicylic acid, and sodium polystyrene sulfonate (PSS) standards (Scientific Polymer Products Inc, Ontario, NY) with molecular weights of 1.6, 5.2, 7.4, 16, and 34 kDa. Prior to HPSEC analysis, samples were filtered with a 0.45 µm membrane filter and adjusted to an ionic strength similar to the mobile phase using sodium chloride.

Results and Discussion

Effect of preozonation on raw surface water

Table 4-2 shows a variety source water quality parameters and how they were affected by ozone. Preozonation at 0.70 mg O_3/mg DOC initially removed approximately 5% of the DOC. The pH and conductivity were not significantly affected. True color was reduced by approximately 56%. The aromaticity of the remaining DOC was reduced as indicated by specific UV absorbance (SUVA) which dropped from 4.3 to 3.1 L/mg-m.

Table 4-2: Comparison of water quality from both the preozonation experiment and the experiment without preozonation.

Parameter	Without Preozonation			With Preozonation		
	Raw	Raw → coagulation (Post-CFS)	Raw → coagulation → UF (UF Filtrate)	Raw → ozone	Raw → ozone → coagulation (Post-CFS)	Raw → ozone → coagulation → UF (UF Filtrate)
pH	6.8	6.3	6.4	6.8	6.2	6.2
Dissolved Oxygen (mg/L O_2)	8.0	8.3	8.4	12.1	10.3	10.4
Turbidity (NTU)	2.2	1.6	0.1	1.8	2.9	0.1
Conductivity (μS/cm)	186	209	209	192	208	209
True Color (PCU)	180	15	15	79	8	9
DOC (mg/L)	19	7	7	18	9	9
UV_{254} (cm^{-1})	0.85	0.19	0.19	0.56	0.17	0.17
SUVA (m-L/mg)	4.3	2.6	2.7	3.1	1.9	2.0

UV-Vis wavelength scans are presented in Figure 4-3. These scans indicated that ozone had the most significant impact on UV absorbance wavelengths between 200 nm and 250 nm. As expected, these results suggested that ozone preferentially destroyed or broke down the aromatic-rich, UV absorbent fraction of the dissolved organic matter found in the raw Lake Manatee surface water.

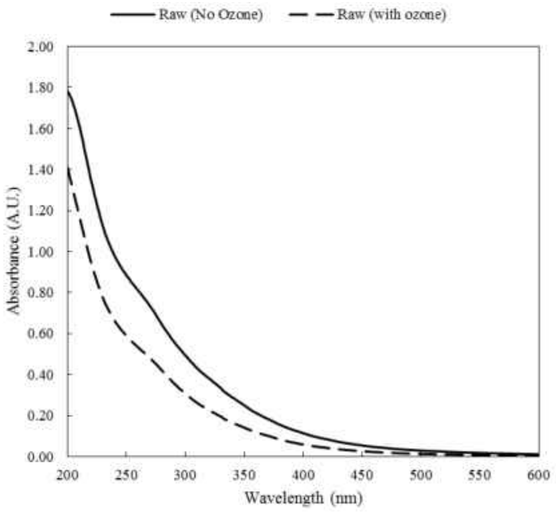

Figure 4-3: UV-Vis absorbance scans for Raw and Ozonated Surface Water

Figure 4-4 presents the EEM data both before and after ozonation. The raw surface water EEM presented in The various peaks shown in Figure 4-4, part A suggested that the source water contained aromatic protein-like, humic acid-like, and fulvic acid-like substances. Figure 4-4, part B revealed that the presence of these fluorescing substances had been diminished following ozonation as expected.

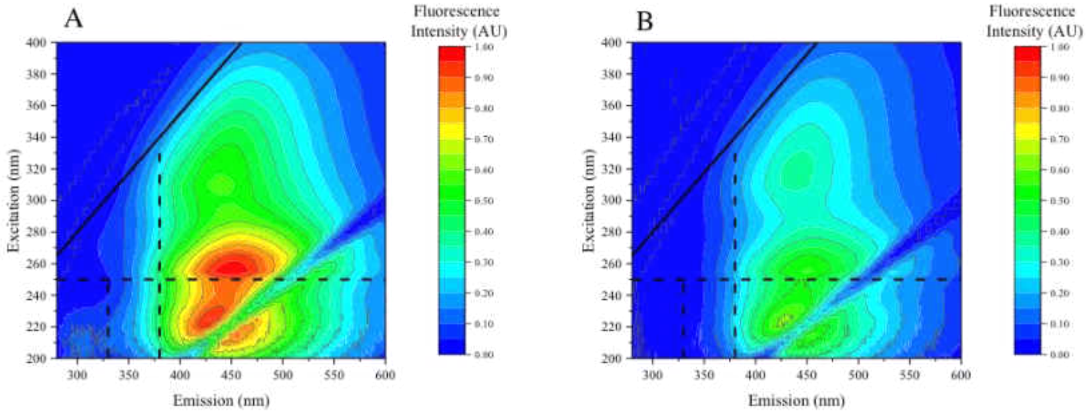

Figure 4-4: EEMs of raw (A) and ozonated (B) surface water.

This difference was quantified using the EEM spectra FRI analysis (shown in Figure 4-5) which revealed that the greatest magnitude of reduction in integrated fluorescence intensity was from the fulvic-acid like region (Region III).

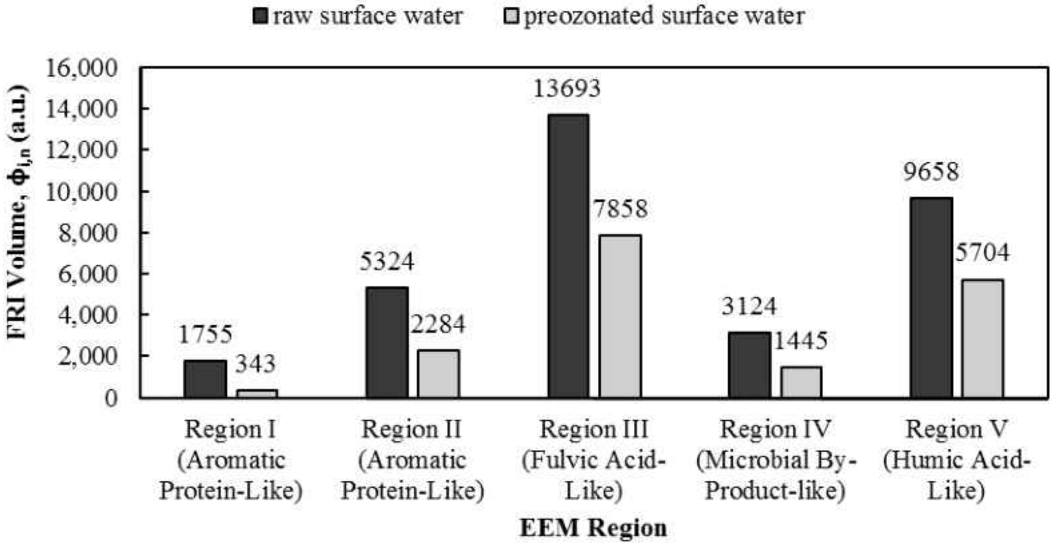

Figure 4-5: Results of the FRI analysis for raw surface water and preozonated surface water.

However, while Region I (aromatic proteins) exhibited the least fluorescence, it experienced the greatest percent reduction (approximately 80%). Likewise, Region II (aromatic proteins) also experienced a 57% reduction in fluorescence. As a result, Region III and V (humic-like substances) became relatively more predominant than Regions I, II, and IV in the ozonated samples compared to the raw surface water albeit at significantly lower magnitudes.

These results suggest that ozone preferentially removed fluorescent organic compounds from the raw surface water as expected. However, given that only 5% of the DOC was removed from the water, the characteristics of the organics matter fed to the coagulation step were significantly altered when preozonation was applied.

The average apparent molecular weight of the UV absorbing organic matter was reduced as a result of preozonation. The results of the HPSEC chromatograph (Figure 4-6) revealed that the preozonated water had a broader distribution of molecular weights compared to the unozonated raw water due to the broader shape of the preozonated surface water peak.

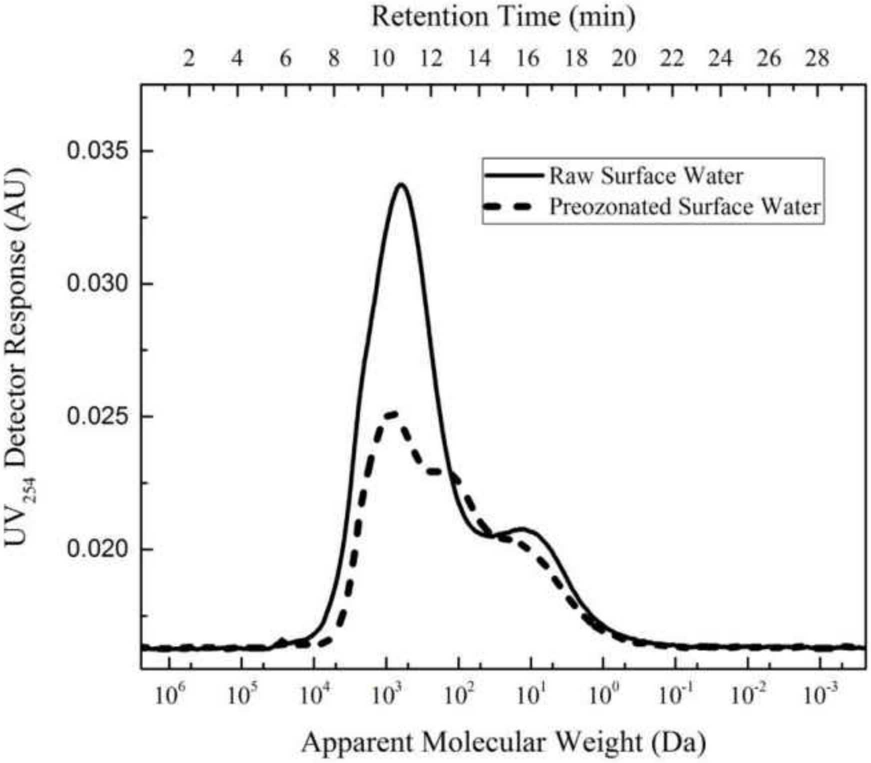

Figure 4-6: HPSEC apparent molecular weight distribution for raw surface water and ozonated surface water.

Analysis of the HPSEC data revealed that the weight-averaged apparent molecular weight of the raw surface water was 952 Da compared to 693 Da in the ozonated surface water (a 27% reduction) which confirmed that preozonation broke down the organic matter found in the raw water to compounds of smaller molecular weight.

Effect of preozonation on post-coagulation water quality

While the direct impact of ozone on the surface water were not surprising, the results of the bench-scale study revealed significant differences in the CFS process performance when preozonation was implemented. In the experiment with preozonation, the CFS process improved with respect to removal of color removal. The post-CFS true color was 8 compared to 15 when treated without preozonation. However, when assessed as a percent removal, the CFS performance for color removal was unchanged at approximately 90% true color removal in both cases. A similar trend applied to UV_{254} absorbance removal. Applying preozonation led to a lower post-CFS UV_{254} absorbance, however, the percent removal was only slightly reduced. CFS removed approximately 80% of the UV absorbance from the raw surface water and achieved approximately 70% removal from the ozonated surface water. Fluorescent EEMs indicated that the post-CFS water had reduced fluorescence when preozonation was applied as shown in Figure 4-7. However, turbidity and DOC were both found to be at higher levels in the post-CFS samples when preozonation was applied indicating that ozone had impaired the performance of the CFS process for turbidity and overall organics removal. Smaller floc, that settled more slowly were observed when treating preozonated water which was an additional indicator of impaired coagulation performance. However, the application of preozonation led to a reduced the aromaticity of the post-coagulation water. The post-CFS samples from the preozonation experiment had a SUVA of approximately 1.9 L/mg-m compared to 2.6 L/mg-m without preozonation.

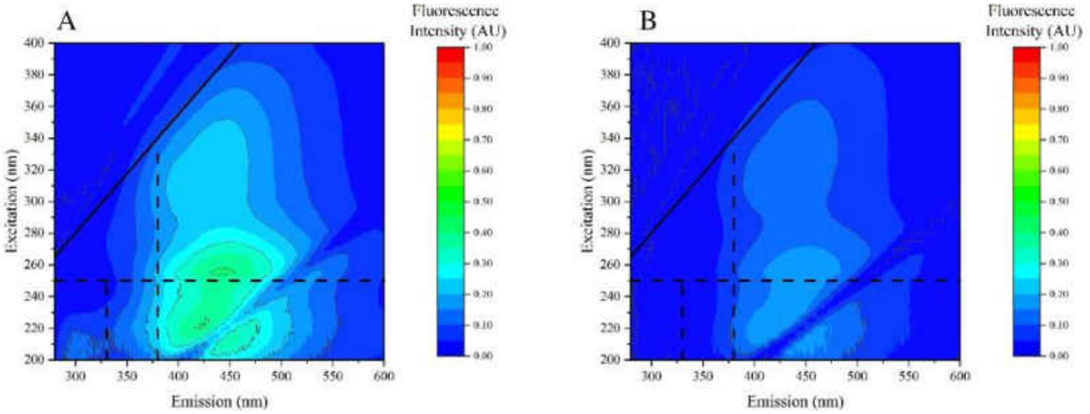

Figure 4-7: EEM data for post-coagulation water without preozonation (A) and with preozonation (B)

Effect of preozonation on filtrate water quality

These trends mostly carried forward into the filtrate samples. DOC was found to be at a higher concentration for filtrate samples from the preozonation experiment. However, the SUVA, true color, and fluorescence (Figure 4-8) were reduced in the filtrate water produced during the preozonation study. These results suggested that the reduction of aromatic-rich, and fluorescent compounds from preozonation was consistent in the post-CFS water but the reduction in turbidity and DOC due to preozonation did not carry forward beyond the preozonation step due to the adverse impact to the CFS process from the integration of preozonation.

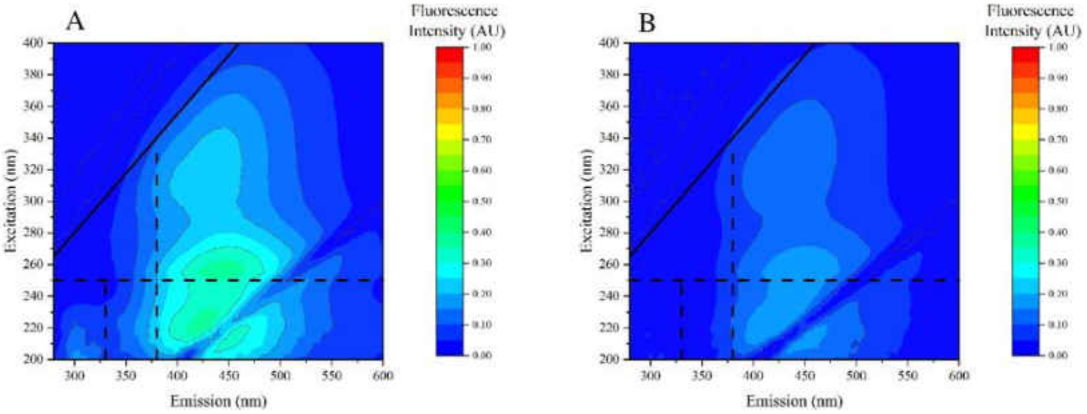

Figure 4-8: EEM data for UF filtrate water without preozonation (A) and with preozonation (B).

Effect of preozonation on membrane fouling

Finally, in order to assess the changes in organic fouling due to the integration of ozone and coagulation, differential EEMs were calculated and are presented in Figure 4-9. The differential EEMs represent a subtraction of the filtrate EEM from the post-CFS EEM, and therefore are representative of fluorescent compounds that were retained by the ultrafiltration membrane. While Figure 4-7 and Figure 4-8 showed that the quantity of fluorescing organic material was less throughout the process with preozonation, Figure 4-9 showed that the fluorescing substances were no longer being retained by the membrane.

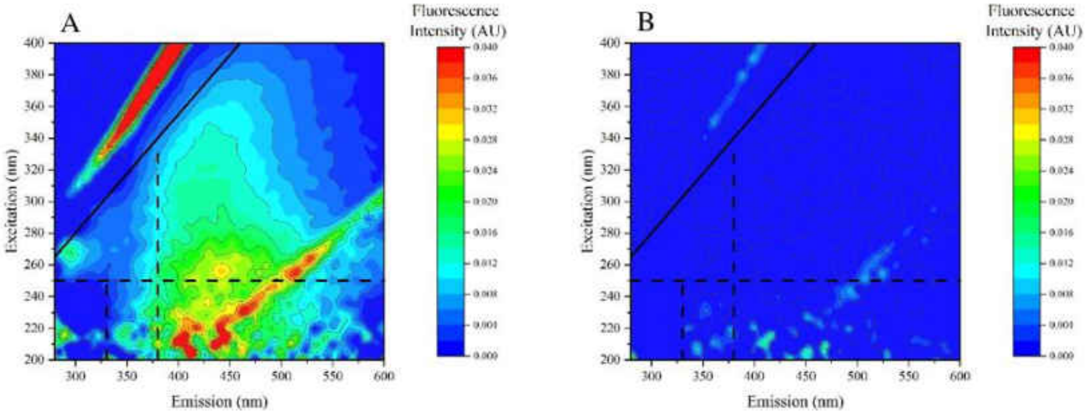

Figure 4-9: Differential EEMs (Feed-Filtrate) for the experiment without preozonation (A) and with preozonation (B)

In other words, the DOC in the process with preozonation was less fluorescent, less aromatic, and less retained by the membrane. However, there was approximately 28% more DOC in the filtrate water when using preozonation as compared to the control. However, this increase in filtrate DOC was apparently due to the impaired CFS process, not because additional organics were passing through the membrane.

Likewise, the differential UV-Vis absorbance scans presented in Figure 4-10 were calculated by subtracting the filtrate UV-Vis absorbance scan data from the post-coagulation absorbance scan data. These plots illustrate the magnitude of the additional organics retained by the membrane during the control experiment without preozonation. While the DOC analysis was not precise enough to quantify the removal of DOC by the ultrafiltration membrane, the differential EEMs presented in Figure 4-9 and the differential absorbance scans in Figure 4-10 were sensitive enough to detect a change retained organics retained on the ultrafiltration membrane. Given that aromatic, fluorescent compounds are known to cause chemically irreversible fouling, preozonation integrated with coagulation and ultrafiltration may yield a more chemically reversible type of fouling. These results seem to indicate that although the DOC was elevated in the water treated with preozonation followed by coagulation, fluorescent organic matter known to cause irreversible fouling (such as humic substances) were not retained by the membrane. These EEM results would suggest that less chemically irreversible foulants were in the feed water during the experiment with preozonation. Therefore, future research should investigate how application of preozonation can alter chemically irreversible fouling of membranes used in conventional surface water treatment.

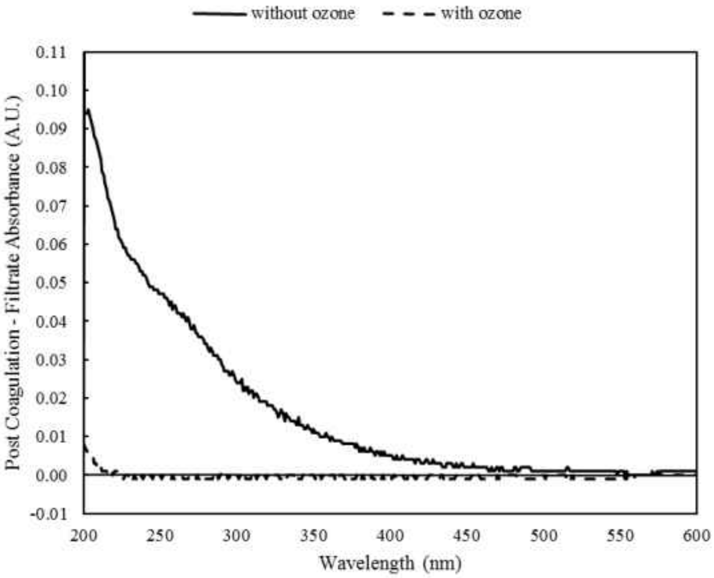

Figure 4-10: Differential absorbance scans (Feed-Filtrate) for the experiment without preozonation and with preozonation

Conclusions

The goal of this work was to investigate the impact of integrated preozonation and coagulation on organic fouling. The major findings of this study are as follows:

- Preozonation at 0.70 mg O_3/mg DOC initially removed only 5% of the DOC, but a significant fraction of the humic acid-like, fulvic acid-like and protein-like substances known to cause irreversible membrane fouling were removed.
- Preozonation at 0.70 mg O_3/mg DOC, integrated with PACl coagulation, enhanced the overall removal of turbidity, color, UV_{254} absorbing constituents, and fluorescent constituents in surface water. However, DOC increased in the UF feed by 28% due to impaired removal of DOC by CFS.
- Differential EEMs and absorbance scans confirmed that the remaining aromatic, fluorescent fraction of the organic matter was no longer retained on the membrane when preozonation was integrated with coagulation.
- Future research should investigate the changes in the long-term, chemically irreversible fouling rate of surface water pretreated with ozone and coagulation to further assess this integrated treatment configuration.

Acknowledgments

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CHAPTER 5: MONITORING THE FATE OF FLUORESCING SUBSTANCES RECYCLED IN ULTRAFILTRATION PROCESS BACKWASH WATER

Abstract

The fate of fluorescing substances during the recycling of membrane backwash water (MBWW) ahead of coagulation, flocculation and sedimentation (CFS) with ultrafiltration (UF) membranes has been investigated. Bench-scale UF membranes were used to generate MBWW from a CFS-treated surface water containing 21 mg/L dissolved organic carbon (DOC) registering a 0.95 cm^{-1} UV_{254} absorbance that had been coagulated with 100 mg/L with polyaluminum chloride. CFS settled water, when processed with UF, produced MBWW containing 9 mg/L DOC registering a 0.25 cm^{-1} UV_{254} absorbance. High performance size-exclusion chromatography using UV_{254} detection demonstrated an analogous UV_{254} reduction as measured by detector response. However, fluorescence excitation emission spectroscopy revealed that protein-like substances, known to be associated with irreversible fouling, had been concentrated in the MBWW. In order to evaluate recycling operations on overall DOC removal in a CFS-UF process, a blend of 30% MBWW with 70% of raw water was treated, resulting in an overall DOC removal of 73%. However, without MBWW recycle, the CFS-UF process removed less of the influent DOC (63%). This work suggests that MBWW recycle operations should consider possible downstream impacts of concentrated protein-like substances not previously detected, as these substances are suspected to contribute to long-term irreversible UF fouling.

Introduction

The replacement of traditional granular media filters with hollow fiber ultrafiltration (UF) membranes for conventional drinking water treatment filtration can result in more consistent finished water quality with increased rejection of natural organic matter (NOM) (Farahbakhsh et al. 2004, Zularisam et al. 2009). As a result, membrane filtration is considered an important and widely used process in surface water treatment, and desalination processes. However, a key barrier to more widespread adoption of UF membranes continues to be membrane fouling caused by NOM (Gao et al. 2011, Huang et al. 2009). Hydraulic and chemical backwashing can be utilized to mitigate the effects of organic fouling but, if used excessively, these processes can reduce the efficiency of the treatment system since filtered water is wasted when backwashed. Many utilities recycle hydraulic membrane backwash water (MBWW) to reduce waste. However, the impact of recycling MBWW on the performance of both coagulation and membrane processes is not well understood.

In conventional surface water treatment (coagulation-flocculation-sedimentation-media filtration), the recycling of granular media filter backwash water (FBWW) to the headworks of the treatment plant is commonly practiced to reduce waste (Gouellec et al. 2004). Cornwell (2001) found through a survey of over 500 water plants that 44% of the plants recycled some type of waste stream. This survey also revealed that *Giardia* and *Cryptosporidium* were detected in FBWW at concentrations 16 to 21 times higher than the corresponding source water raising concerns about the potential for oocysts to accumulate in the within the treatment process. Backwash water has also been characterized as having elevated concentrations of total suspended solids, total organic carbon and inorganic constituents that are found in the raw water (Cornwell 2001, Tobiason et al. 2003). Additionally, Cornwell (2001) noted that chemical precipitates from the use of coagulants are also concentrated in backwash water. Gottfried et al. (2008) demonstrated that recycling FBWW can increase NOM removal by enhancing coagulation since FBWW contains destabilized particles. As a result, their work also showed that coagulant dosing requirements may be reduced when recycling FBWW.

Research has also been conducted to assess the treatability of FBWW and to determine what intermediate processes would be necessary to prevent an accumulation of *Giardia* and *Cryptosporidium* as a result of recycling FBWW (Arora et al. 2001, MacPhee et al. 2002). In response to the results of these studies, and in an effort to protect the public from the accumulation of contaminants in this waste stream, the U.S. Environmental Protection Agency developed federal regulations, such as the Filter Backwash Recycling Rule (FBRR), that requires recycled FBWW to be returned to the head of the water treatment plant (Environmental Protection Agency 2002). The FBRR also requires utilities to keep records of its recycling practices and to report them to their state government. Furthermore, the FBRR also provides guidance that recommends limiting the recycle of backwash water to 10% to reduce the likelihood of an accumulation of oocysts in the main treatment process. Research has continued on FBWW regarding disinfection-by-products (McCormick et al. 2010, Walsh et al. 2008) and NOM removal (Suman et al. 2012). However, despite recent adoption of membranes in water treatment, there is little guidance on how to handle MBWW recycling and the research conducted to develop the FBRR guidance did not include consideration of dissolved organic contaminants that could act as foulants to a membrane system. Zhou et al. (2013) characterized and tracked the properties of the NOM found in FBWW through analysis of its molecular weight distribution, hydrophobicity, and fluorescence. This analysis revealed that recycling FBWW could improve overall dissolved organic carbon (DOC) removal but led to increased protein-like matter in treated water. This protein-like matter would be of concern for a membrane process because research has shown that bio-polymers consisting of protein-like substances are known to cause irreversible fouling in ultrafiltration membranes (Haberkamp et al. 2011, Peiris et al. 2013, Yamamura et al. 2014).

However, most research on MBWW has been focused on the potential impacts to finished water quality (Gouellec et al. 2004, McCormick et al. 2010, Walsh et al. 2008) or impacts to the efficiency of the coagulation process (Boyd et al. 2012, Gora and Walsh 2011). In one such study, Boyd et al. (2012) determined that carboxylic acids used in chemical backwashes were present in some MBWW and could interfere with coagulation if recycled. While this work demonstrated a potential challenge with regards to recycling MBWW, Gora and Walsh (2011) demonstrated that similar to improved organic removal through coagulation was achieved when the water was initially blended with 10% FBWW or MBWW. Limited research has been conducted on the possibility of recycling backwash water reintroducing concentrated dissolved foulants back into the treatment system. In the bench-scale work conducted by Cornwell (2001), increased fouling of MF membranes was observed when treating SFBW and concluded that pilot work would be required to further investigate the fouling. Khramenkov et al. (2011) reported that NOM accumulation from SFBW had occurred in a full-scale conventional treatment system which used ultrafiltration membranes. In their study, a complete discharge of backwash water was tested which resulted in a 10% increase in permeability after only two days. Gora and Walsh (2011) did not observe an increase in transmembrane pressure when testing the impact of recycling backwash water at 10% for a bench-scale outside-in UF membrane. However, the focus of their study was on the impact to permeate quality and they concluded that future research would be necessary to assess the impact of recycled MBWW on membrane fouling.

The purpose of this research was to evaluate the impact of recycling MBWW on coagulation performance and membrane filtration. Advanced DOC characterization techniques including fluorescent excitation-emission spectroscopy and high-pressure size exclusion chromatography (HPSEC) were applied to identify and compare the components of DOC in processes impacted by recycled MBWW.

Materials and Methods

Source water

Untreated surface water was collected from the Lake Manatee Water Treatment Plant in Manatee County, Florida. This source water was chosen because it is currently treated through conventional surface water treatment with media filtration but is slated to transition to ultrafiltration membranes (Sethi et al. 2015).

Bench-scale hydraulic backwashing

The bench-scale assessment of MBWW recycling was conducted in two phases. In the first phase, a solid-contact clarification system was simulated by dosing raw surface water with polyaluminum chloride (PACl) coagulant in a jar tester. The coagulant dose of 100 mg/L PACl was chosen based off of information provided by the Lake Manatee Water Treatment Plant. The jar testing apparatus (Phipps and Bird, Richmond, VA) used to conduct the test contained six jars that were filled with two liters of raw surface water in each jar. The jar testing sequence was chosen to match the conditions of a surface water treatment plant that utilizes a solid-contact clarifier. This sequence consisted of 11 seconds at 300 rpm to simulate a rapid mix, 4 minutes and 14 seconds at 100 rpm to simulate mixing at the inlet works, 8 minutes at 60 rpm to simulate the clarifier mixing zone, 7 minutes at 5 rpm to simulate the clarifier flocculation zone, and 10 minutes at 0 rpm to simulate settling.

The supernatant or settled water from these jar tests (denoted as “post-CFS”) were collected in a single 5-gal bucket used to feed the bench-scale hollow fiber UF membrane. The bench-scale hollow-fiber UF membrane composed of a blend of polyethersulfone and polyvinylpyrrolidone. The bench-scale membrane module was operated with an inside-out, dead end flow path. The module contained a total of 120 fibers which made up a combined of 0.08 m^2 of total active area. Each fiber had a 0.8 mm diameter and were 300 mm in length. The nominal pore size of the membrane was 0.010 µm (0.025 µm absolute) and the molecular weight cut-off was 200,000 Da. The filtration experiments were carried out by pumping feed water to a membrane module using a peristaltic pump. A thermocouple, pressure transducer, and digital flow meter connected to a data acquisition system were used to collect operational data during the experiments.

A permeate flux of 85 L/m-hr (50 gal/sf-day) was maintained during filtration. Hydraulic backwashing with filtrate at 255 L/m-hr for 60 seconds was conducted after approximately 45 minutes of filtration. Six backwashes occurred throughout this phase of testing. The MBWW from each filtration cycle combined in a single reservoir.

Bench-scale MBWW recycling

In the second phase of work, the jar tests were repeated, however, three of the jars contained 30% MBWW and 70% raw surface water, while the other three jars contained 100% raw surface water. This recycle blend ratio was chosen to exaggerate the effect of recycling MBWW so that water quality changes as a result of recycling MBWW would be amplified.

Additionally, the membrane fouling potential of the post-CFS samples were assessed using flat-sheet ultrafiltration membranes. Polyethersulfone membrane disks with a 0.03 μm absolute pore size and a 47 mm diameter were used for the ultrafiltration tests conducted in this phase of work. These membranes were first rinsed with approximately 20 mL of distilled water. A vacuum pump operated at 10 psi was then used to filter 100 mL of sample water. A timer was used to determine how much time was required to filter 100 mL sample. This time was compared to a baseline filtration time established by filtering 100 mL of distilled water. The filtration times were compared to assess the impact of recycled MBWW on membrane fouling potential.

Analytical methods

The samples collected during the bench-scale experiments were tested for water quality parameters including pH, turbidity, temperature, and conductivity in accordance with standard methods (APHA et al. 2005). Additional parameters which relate to organic characterization were determined including DOC, UV-Vis spectra, true color in platinum cobalt color units (PCU), the apparent molecular weight distribution, and fluorescence excitation-emission spectra.

DOC was determined after filtering samples with a pre-washed 0.45 µm membrane filter followed by analysis using a Fusion Total Organic Carbon Analyzer (Teledyne Tekmar Inc, Mason, OH) according to Standard Method 5310C (APHA et al. 2005). UV-Vis spectra were analyzed using a DR5000 spectrophotometer (Hach, Loveland, CO). Samples were first filtered through a pre-washed 0.45 µm membrane filter before undergoing UV-Vis scans. Each scan was conducted from wavelength 200 nm to 600 nm in 1-nm intervals.

Fluorescence excitation-emission spectroscopy was conducted to further characterize the dissolved organic matter. Prior to fluorescence analysis, samples were filtered with a 0.45 µm membrane filter to remove particulates. Without further pretreatment, fluorescence excitation-emission matrix (EEM) spectra were collected using a Shimadzu RF-6000 spectrofluorophotometer (Kyoto, Japan). The emission intensity readings were captured in 1-nm wavelength intervals between 280 nm and 600 nm for excitation wavelengths ranging from 200 nm to 400 nm in 5-nm intervals. The excitation and emission slits were set to a 10-nm band-pass.

The effect of Raleigh scattering was reduced by subtracting the fluorescence spectra collected from a sample of deionized water. Given that the organic content of the surface water was thought to potentially contain more than 20 mg/L for some samples, it was also important to account for the absorption of light by the DOC of the sample (commonly referred to as the inner filter effect). A correction for the inner filter effect was applied to the blank-subtracted spectra following the method described by Westerhoff et al. (2001).

A data analysis technique developed by Chen et al. (2003) referred to as Fluorescence Regional Integration (FRI) was used to quantify and compare the results of each EEM sample taken. FRI involves dividing an EEM into characteristic regions and subsequently determining a normalized, integrated volume ($\phi_{i,n}$) for each region. A legend of the regions utilized in this study is described in Table 5-1 and illustrated in Figure 5-1.

Table 5-1: Description of FRI regions

EEM Region	Excitation Range	Emission Range	Description
Region I	200 – 250	280 – 330	Aromatic Protein-Like
Region II	200 – 250	330 – 380	Aromatic Protein-Like
Region III	200 – 250	380 – 600	Fulvic Acid-Like
Region IV	250 – 340	280 – 380	Soluble Microbial By-Product-Like
Region V	250 – 400	380 – 600	Humic Acid-Like

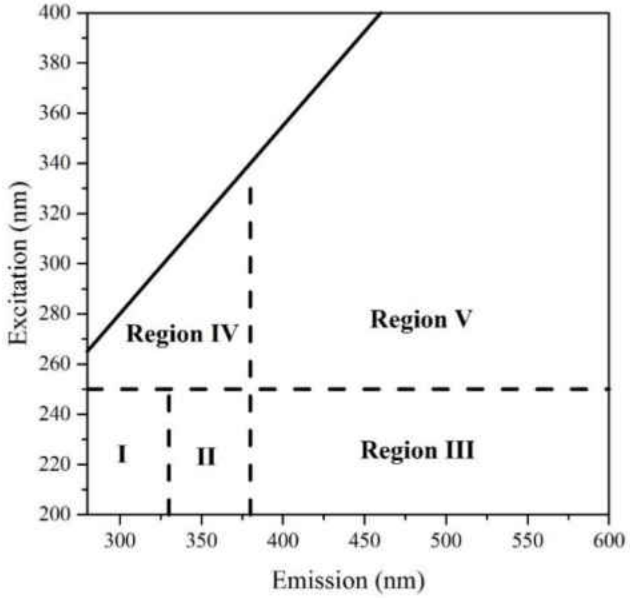

Figure 5-1: Fluorescence Regional Integration legend

The apparent molecular weight distribution (AMW) of the natural organic matter was determined using high-performance size exclusion chromatography (HPSEC). The details of the HPSEC method employed are provided in detail elsewhere (Chin et al. 1994, Zhou et al. 2000). In brief, a Perkin Elmer Series 200 HPLC system consisting of a pump and autosampler were used. The mobile phase was a phosphate buffer that consisted of 2mM K_2HPO_4, 2mM KH_2PO_4, and 0.1 M NaCl. The mobile phase was pumped at a flow rate of 1 mL/min. The sample injection volume was 150 µL. The size exclusion column used was a Protein-Pak 125 (Waters Inc, Milford, MA). Calibration was achieved with molecular weight standards prepared from HPLC-grade acetone, salicylic acid, and sodium polystyrene sulfonate (PSS) standards (Scientific Polymer Products Inc, Ontario, NY) with molecular weights of 1.6, 5.2, 7.4, 16, and 34 kDa. Prior to HPSEC analysis, samples were filtered with a 0.45 µm membrane filter and adjusted to an ionic strength and pH similar to the mobile phase using sodium chloride, K_2HPO_4, and KH_2PO_4 to prevent undesired interactions between the sample and the column media that would exaggerate retention times.

Results and Discussion

MBWW and raw water characteristics

Raw water surface water was jar tested (without blending recycled MBWW) which reduced the DOC from approximately 21 mg/L to 7.3 mg/L, or 65% removal. The UV_{254} absorbance, specific UV_{254} absorbance (SUVA), true color, turbidity, and other water quality measurements taken during this test are shown in Table 5-2.

Table 5-2: Water Quality Data from MBWW backwashing

Parameter	Raw Water	Post-CFS	Hollow Fiber UF Filtrate	Hollow Fiber UF Backwash
pH	6.6	5.8	5.9	6.0
Turbidity (NTU)	2.35	2.03	0.06	16.6
Conductivity (µS/cm)	157	188	188	230
True Color (PCU)	202	17	16	<5
DOC (mg/L)	21	7.3	7.3	9.9
UV_{254} (cm^{-1})	0.95	0.20	0.19	0.25
SUVA	4.5	2.7	2.6	2.5

The backwash water quality shown in Table 5-2 is for the combined backwash water collected from the six backwash events that took place during the testing. While the backwash water did have a relatively high turbidity of 16.6 NTU, the MBWW initially did not appear to have dissolved components that were concentrated higher than the raw surface water. The UV_{254}, DOC, and true color were lower in the MBWW than in the raw water. The DOC in the MBWW was 9.9 mg/L C which was higher than the 7.3 mg/L C found in the filtrate. However, the SUVA was slightly reduced in MBWW indicating that the organics concentrated in the MBWW were of similar overall aromaticity compared to the filtrate.

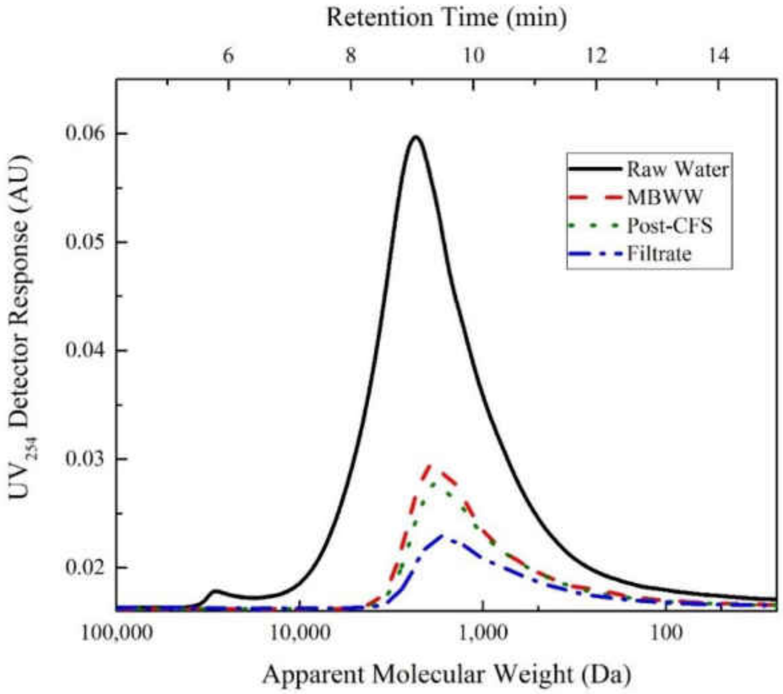

Figure 5-2: HPSEC chromatograph showing apparent molecular weight distribution of raw water, MBWW, Post-CFS, and filtrate.

HPSEC results shown in Figure 5-2 revealed that the apparent molecular weight distribution of UV_{254} absorbing constituents in MBWW was similar to that of the post-CFS samples. The magnitude of the HPSEC response was below that of the raw water suggesting that there was no particular size fraction of UV_{254} absorbing constituents present at a higher concentration than the raw surface water. Overall, the HPSEC results demonstrated an analogous UV_{254} difference between the raw surface water and the MBWW. This suggested that the MBWW did not contain a particular size-fraction of UV_{254} absorbing components that was concentrated relative to the raw water.

However, the fluorescent EEMs, shown in Figure 5-3A and Figure 5-3B, revealed that protein-like substances (regions I and II) were in fact concentrated in the MBWW and were clearly producing a higher response than in the raw surface water. This concentration is quantified by the FRI integrated volumes ($\phi_{i,n}$) shown in Figure 5-4.

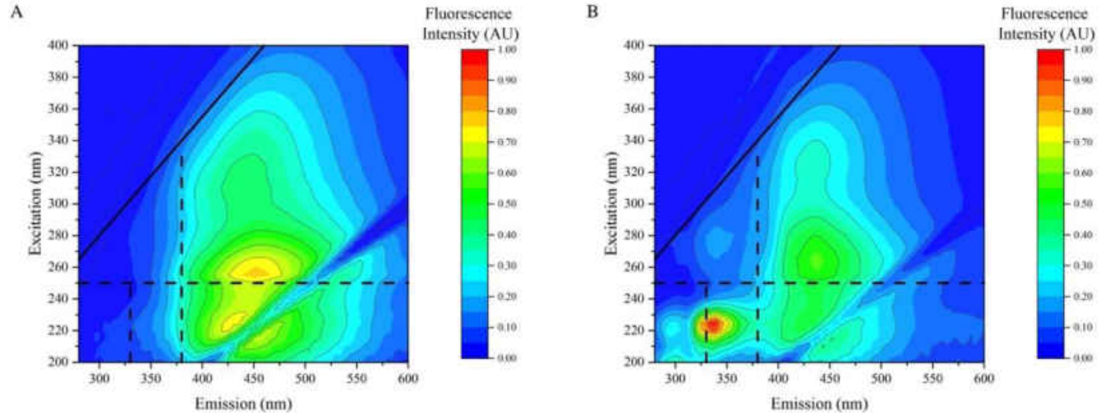

Figure 5-3: Fluorescence EEMs for raw water (A) and MBWW (B)

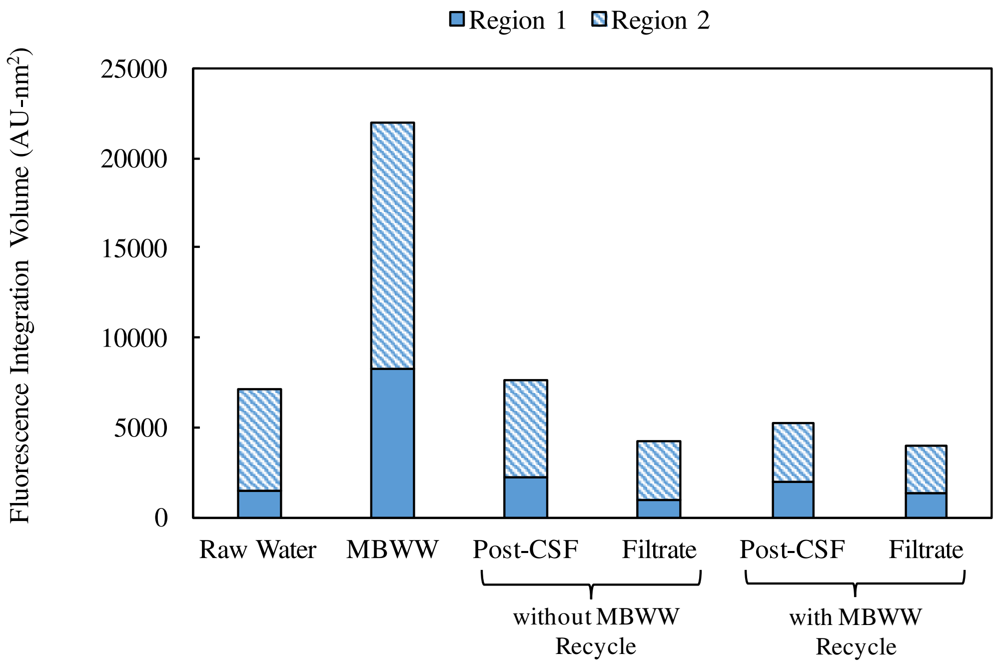

Figure 5-4: Normalized regional integration, $\varphi_{i,n}$ for regions I and II

Effect of MBWW recycle

In the second phase of testing, the jar testing was repeated with a 30% recycle of MBWW revealing an increased removal of turbidity, true color, DOC, and UV$_{254}$ absorbance as shown in Table 5-3. As seen in Figure 5-5A and Figure 5-5B, the post-CFS samples from the test with recycle showed reduced fluorescence compared to the post-CFS from the test without recycle. This indicated that the incorporation of membrane backwash water improved removal of fluorescent organic compounds. DOC removal was 63% during the test without recycle and was 73% during the test with recycle. Notably, the EEMs from this set of jar tests revealed that the coagulation process with MBWW recycle removed protein-like substances to a greater degree than the control test without MBWW recycle. As a result, the protein-like substances did not accumulate in the overall bench-scale treatment system with MBWW recycle in with the surface water from Lake Manatee.

Table 5-3: Water quality data from MBWW recycling experiment

	0% Recycled Backwash 100% Raw Water		30% Recycled Backwash 70% Raw Water	
Parameter	Post-CFS	Flat-Sheet UF Filtrate	Post-CFS	Flat-Sheet UF Filtrate
pH	6.2	6.4	5.9	6.2
Turbidity (NTU)	2.71	0.09	1.71	0.06
Conductivity (µS/cm)	231	225	239	233
Apparent Color (PCU)	87	16	48	6
DOC (mg/L)	8.2	7.7	6.1	5.7
UV254 (cm-1)	0.22	0.13	0.14	0.09
SUVA	2.7	1.7	2.3	1.7

Similar results were observed for the UF filtrate samples. As seen in Figure 5-5C and Figure 5-5D, the filtrate samples from the test with recycle showed reduced fluorescence compared to the filtrate from the test without recycle. The DOC in the filtered water from the test without MBWW recycle was 7.7 mg/L C compared to 5.7 mg/L C in the filtrate water from the experiment with MBWW recycle.

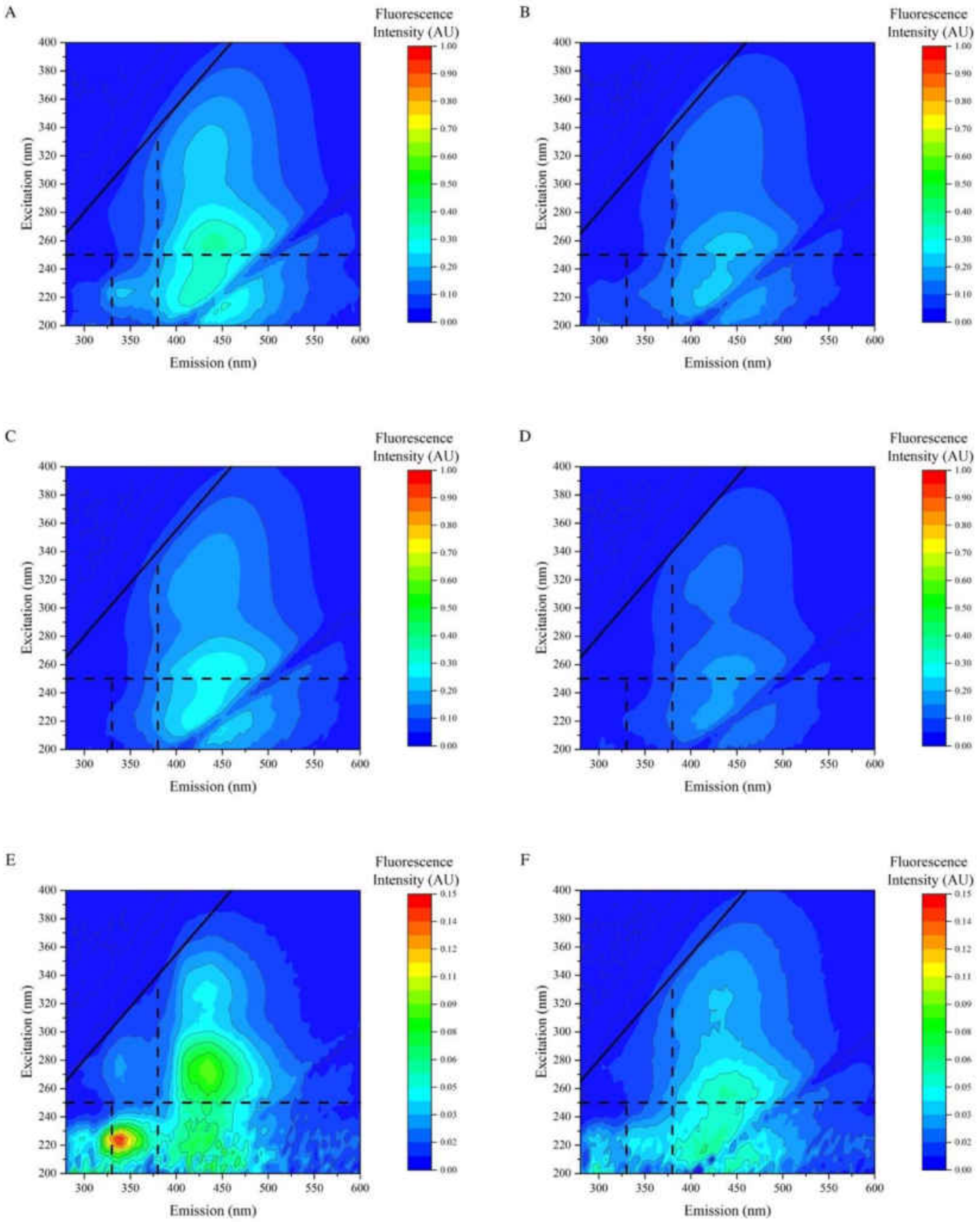

Figure 5-5: Fluorescence EEMs for post-CFS without (A) and with recycle (B), filtrate without (C) and with recycle (D), and differential EEMs, [post-CFS minus filtrate] for samples without (E) and with recycle (F)

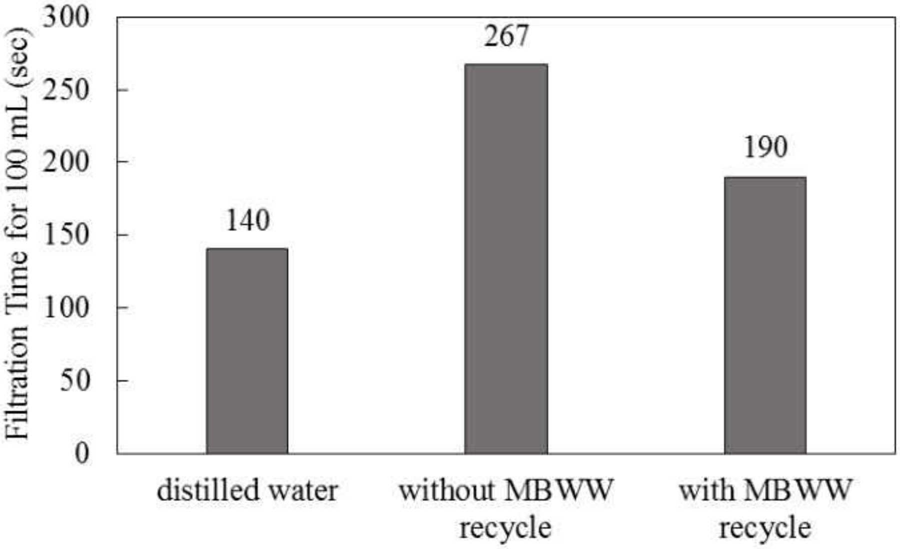

Figure 5-6: Time required in seconds to filter 100 mL of sample through a 0.02 µm flat sheet polyethersulfone membrane filter at 10 psi vacuum pressure.

Flat sheet ultrafiltration testing results shown in Figure 5-6 revealed a 30% improvement in filterability for the test with MBWW recycle. This result, agreed with the results shown in the differential EEMs. Differential EEMs were calculated by subtracting the filtrate EEM from the associated post-CFS EEM are shown in Figure 5-5E and Figure 5-5F for testing without and with recycled MBWW respectfully. These plots illustrate the types of organic compounds that were retained by the membrane. Less organic matter was retained on the flat sheet membrane during the recycle experiment. Notably, the protein-like substances peak shown on the differential EEM for the test without MBWW recycle (Figure 5-5E) corresponds to the peak found in the MBWW in regions I and II (Figure 5-3B). This provides additional evidence that the protein-like substances were being concentrated in ultrafiltration backwash water due to their tendency to be selectively rejected by during filtration. However, their subsequent removal during CFS indicate that a 30% recycle blend under the conditions tested in this study would not likely lead to protein-like substance accumulation. However, the detection of concentrated dissolved foulants in MBWW nevertheless suggests that future research should further investigate their fate in under additional treatment scenarios.

Conclusions

In this research, the fate of protein-like substances during the recycling of membrane backwash water (MBWW) ahead of coagulation, flocculation and sedimentation (CFS) with ultrafiltration (UF) membranes was investigated. The major findings of this study are as follows:

- MBWW generated during the bench-scale testing was concentrated with protein-like substances suspected to be associated with membrane foulants.
- Recycling MBWW at a 30% blend ratio improved the coagulation process at a PACl dose of 100 mg/L for a surface water containing 21 mg/L DOC.
- The improved coagulation process performance removed concentrated protein-like substances which reduced the likelihood of accumulation occurring as a result of MBWW recycling for the evaluated source water.
- The protein-like substances concentrated in the MBWW were found to be rejected by the ultrafiltration membrane which are known to cause irreversible fouling.

Therefore, caution should be exercised when evaluating the incorporation of MBWW recycle in membrane treatment systems.

- Future research should investigate the fate of protein-like substances under additional treatment scenarios as well as investigate their impact on long-term, irreversible fouling rate of UF membranes used in conventional surface water treatment.

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CHAPTER 6: GENERAL CONCLUSIONS

- Hydraulically irreversible fouling, as indicated by fouling indices, increased with runtime and did not appear to be impacted by changes in pretreatment configuration.

- Normalized specific flux and chemically irreversible fouling of the UF pilot was negatively impacted when the pilot pretreatment configuration switched from the pilot-scale clarifier to the full-scale clarifier suggesting that recycled backwash water may have an impact on membrane fouling.

- Chemically irreversible fouling was poorly correlated with feed turbidity, raw water turbidity, and raw water TOC (<0.70 R^2) suggesting that these surrogate measures of water quality are insufficient to act as pretreatment performance indicators.

- TFI was reduced by 41% when preozonation was applied suggesting that the overall fouling rate had been reduced.

- Preozonation led to improved chemically enhanced backwashes which increased CRFI by 59% and effectively eliminated chemically irreversible fouling.

- Preozonation at 0.70 mg O_3/mg DOC initially removed only 5% of the DOC, but a significant fraction of the humic acid-like, fulvic acid-like and protein-like substances known to cause irreversible membrane fouling were removed.

- Preozonation at 0.70 mg O_3/mg DOC, integrated with PACl coagulation, enhanced the overall removal of turbidity, color, UV_{254} absorbing constituents, and fluorescent constituents in surface water. However, DOC increased in the UF feed by 28% due to impaired removal of DOC by CFS.

- Differential EEMs and absorbance scans confirmed that the remaining aromatic, fluorescent fraction of the organic matter was no longer retained on the membrane when preozonation was integrated with coagulation.

- MBWW generated during the bench-scale testing was concentrated with protein-like substances suspected to be associated with membrane foulants.

- Recycling MBWW at a 30% blend ratio improved the coagulation process at a PACl dose of 100 mg/L for a surface water containing 21 mg/L DOC.

- The improved coagulation process performance removed concentrated protein-like substances which reduced the likelihood of accumulation occurring as a result of MBWW recycling for the evaluated source water.

- The protein-like substances concentrated in the MBWW were found to be rejected by the ultrafiltration membrane which are known to cause irreversible fouling. Therefore, caution should be exercised when evaluating the incorporation of MBWW recycle in membrane treatment systems.

APPENDIX A: ADDITIONAL DIAGRAMS AND PHOTOS

Figure A-1: Photos of the ultrafiltration pilot

Figure A-2: Photo of the pilot-scale solid-contact clarifier

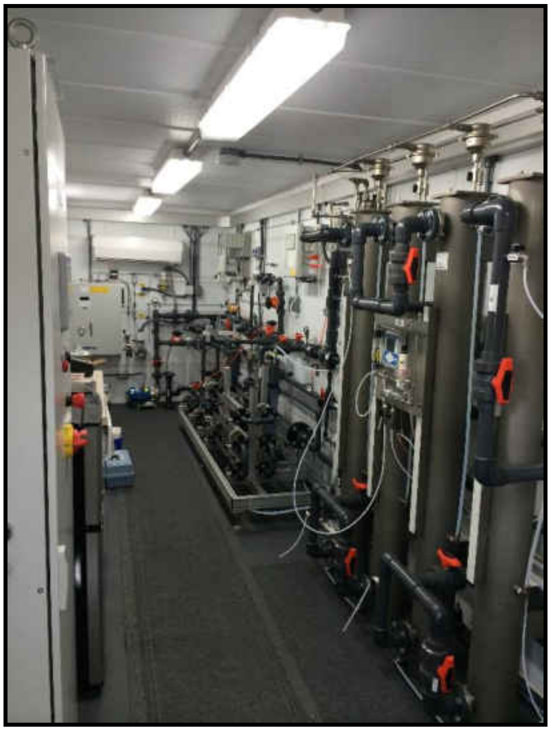

Figure A-3: Photo of interior of the ozone pilot trailer

Figure A-4: Photo of the MSJWTP full-scale solid-contact clarifier

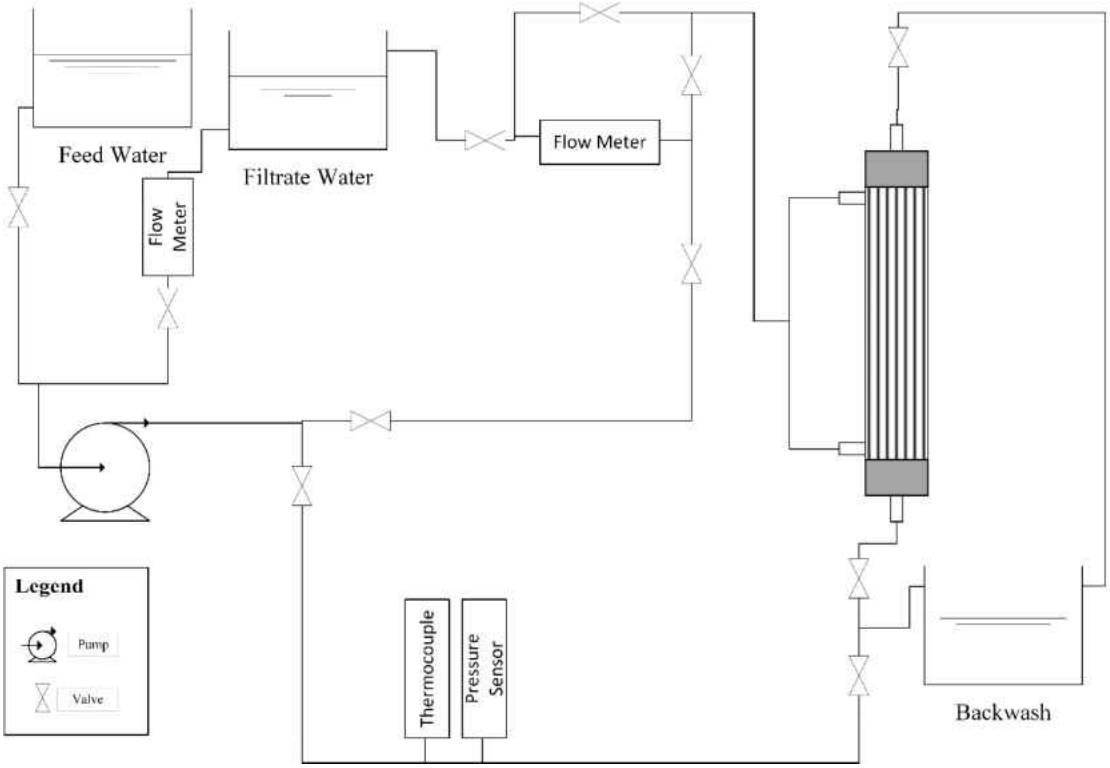

Figure A-5: Process diagram of the bench-scale hollow fiber membrane apparatus

Figure A-6: Photo of the bench-scale hollow fiber membrane apparatus

Figure A-7: Photo of the jar tester apparatus

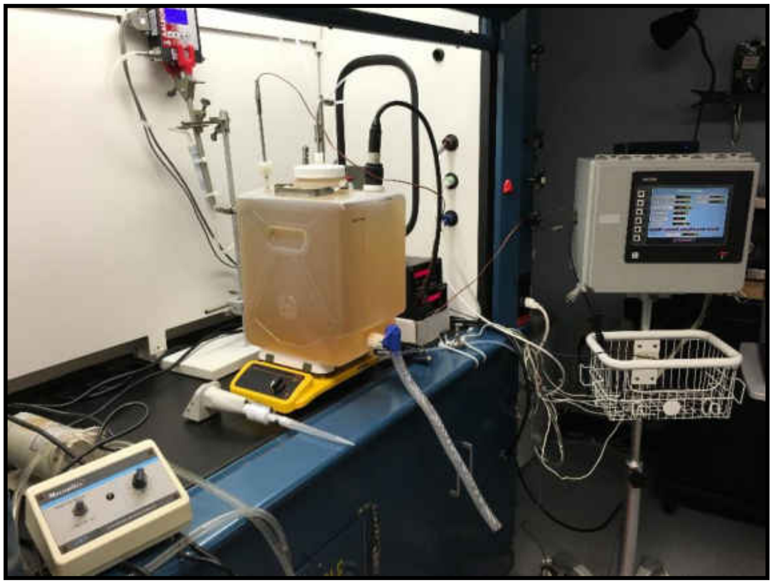

Figure A-8: Photo of the bench-scale ozonation system

APPENDIX B: DAILY-AVERAGE PILOT DATA

Table B-1: Daily Averaged Data from the UF Pilot during forward filtration

CEB Cycle	Filtration Runtime (days)	Feed Turbidity (NTU)	Filtrate Turbidity (NTU)	Temperature (°C)	TMP (psi)
0	0.5	1.74	0.010	20.69	1.79
1	1.2	1.34	0.010	20.58	1.83
2	2.1	1.35	0.010	21.08	1.76
3	3.1	1.41	0.010	21.87	1.72
4	4.0	1.27	0.010	21.83	1.74
5	5.0	1.21	0.010	21.67	1.75
6	6.0	1.37	0.010	22.57	1.74
7	7.2	1.18	0.010	21.94	1.78
8	8.4	1.59	0.010	20.33	1.82
9	9.4	2.29	0.010	19.50	1.79
10	10.4	2.02	0.010	19.70	1.77
11	11.4	1.68	0.010	20.32	1.76
12	12.1	1.35	0.010	20.72	1.75
13	12.8	1.51	0.010	21.00	1.78
14	13.8	1.45	0.010	21.18	1.81
15	14.8	1.63	0.010	21.23	1.83
16	16.2	1.95	0.010	21.52	1.77
17	17.5	2.28	0.010	21.83	1.75
18	18.5	2.23	0.010	22.28	1.74
19	19.5	2.32	0.010	21.77	1.77
20	20.5	2.39	0.010	21.63	1.81
21	21.5	1.96	0.010	22.48	1.77
22	22.5	2.08	0.010	22.19	1.80
23	23.5	2.05	0.010	22.68	1.78
24	24.5	1.88	0.010	24.19	1.72
25	25.5	1.60	0.010	25.01	1.67
26	26.5	1.69	0.010	23.94	1.70
27	27.4	2.69	0.010	22.61	1.76
28	28.4	2.74	0.010	23.11	1.76
29	29.3	3.40	0.010	22.98	1.79
30	30.2	2.59	0.010	22.70	1.83
31	31.1	1.36	0.010	23.24	1.83
32	32.1	1.24	0.010	23.93	1.78
33	33.1	1.10	0.010	24.53	1.73

CEB Cycle	Filtration Runtime (days)	Feed Turbidity (NTU)	Filtrate Turbidity (NTU)	Temperature (°C)	TMP (psi)
34	34.1	1.13	0.010	24.18	1.74
35	34.7	0.77	0.010	23.41	1.72
36	35.2	1.07	0.010	24.01	1.74
37	36.2	0.94	0.010	23.92	1.75
38	37.2	1.16	0.010	23.28	1.81
39	38.2	1.06	0.010	22.64	1.83
40	39.1	1.03	0.010	22.35	1.87
41	40.1	1.01	0.010	22.51	1.88
42	41.1	0.92	0.010	23.43	1.83
43	42.1	0.92	0.010	23.60	1.86
44	43.1	1.01	0.010	23.66	1.90
45	44.1	1.08	0.010	23.16	1.92
46	45.1	1.12	0.010	22.71	1.98
47	46.0	1.36	0.010	23.15	1.98
48	46.9	1.22	0.010	23.58	1.97
49	47.9	1.14	0.010	23.58	1.99
50	48.9	1.17	0.010	24.08	1.96
51	49.9	1.05	0.010	24.54	1.94
52	50.9	1.06	0.010	24.65	1.98
53	51.7	0.98	0.010	25.05	1.98
54	52.7	0.90	0.010	24.24	1.91
55	53.8	1.06	0.010	23.95	1.95
56	54.8	1.18	0.010	23.39	1.99
57	55.8	1.15	0.010	22.82	2.04
58	56.8	1.21	0.010	22.37	2.06
59	57.8	1.27	0.010	22.47	2.05
60	58.8	1.34	0.010	22.37	2.03
61	59.8	1.48	0.010	22.63	2.01
62	60.8	1.41	0.010	23.22	1.99
63	61.8	1.40	0.010	23.03	1.98
64	62.8	1.90	0.010	21.67	2.04
65	63.8	2.63	0.010	21.00	2.07
66	65.2	0.94	0.010	22.28	2.09
67	66.7	1.32	0.010	21.07	2.19
68	67.7	1.66	0.010	20.42	2.18
69	68.6	0.97	0.010	21.51	2.04

CEB Cycle	Filtration Runtime (days)	Feed Turbidity (NTU)	Filtrate Turbidity (NTU)	Temperature (°C)	TMP (psi)
70	69.6	0.85	0.010	22.63	1.94
71	70.6	0.77	0.010	22.63	1.91
72	71.6	0.78	0.010	22.32	1.94
73	72.6	0.81	0.010	22.40	2.03
74	73.6	0.69	0.010	22.26	2.04
75	74.6	0.68	0.010	21.44	2.10
76	75.6	0.76	0.010	20.91	2.12
77	76.6	0.94	0.010	21.37	2.08
78	77.6	0.87	0.010	21.53	2.16
79	78.6	0.89	0.010	22.24	2.24
80	79.6	0.81	0.010	22.44	2.22
81	80.6	0.80	0.010	22.43	2.22
82	81.6	0.80	0.010	22.34	2.23
83	82.6	0.78	0.010	21.49	2.27
84	83.6	0.82	0.010	20.54	2.35
85	84.6	0.83	0.010	19.83	2.46
86	85.6	0.82	0.010	19.59	2.44
87	86.6	0.86	0.010	20.32	2.33
88	87.6	0.83	0.010	20.89	2.34
89	88.6	0.84	0.010	21.05	2.42
90	89.2	0.58	0.010	20.84	2.39
91	89.8	0.81	0.010	20.29	2.51
92	90.7	0.66	0.010	18.79	2.61
93	91.7	0.72	0.010	19.21	2.61
94	92.7	0.78	0.010	20.25	2.61
95	93.7	0.81	0.010	20.58	2.62
96	94.7	0.81	0.010	20.99	2.49
97	95.7	0.83	0.010	21.21	2.28
98	96.7	0.61	0.010	20.17	2.40
99	97.4	0.44	0.010	19.35	2.40
100	98.0	0.58	0.010	19.27	2.50
101	99.0	0.74	0.010	19.07	2.54
102	100.0	0.73	0.010	18.65	2.64
103	100.8	0.97	0.010	18.58	2.71
104	101.6	1.00	0.010	18.55	2.86
105	102.6	1.06	0.010	18.65	2.91

CEB Cycle	Filtration Runtime (days)	Feed Turbidity (NTU)	Filtrate Turbidity (NTU)	Temperature (°C)	TMP (psi)
106	103.4	0.84	0.010	17.79	3.07
107	104.3	0.98	0.010	17.69	3.19
108	105.1	0.92	0.010	18.94	2.05
109	106.0	0.80	0.010	19.00	1.92
110	107.0	0.88	0.010	19.17	1.88
111	108.0	0.89	0.010	18.94	1.87
112	109.0	0.87	0.010	18.36	1.90
113	109.8	0.90	0.010	17.62	1.92
114	110.7	0.79	0.010	17.12	2.01
115	111.7	0.93	0.010	16.97	2.03
116	112.7	0.86	0.010	16.85	2.02
117	113.6	0.82	0.010	16.73	2.02
118	114.4	0.79	0.010	17.17	2.03
119	115.4	0.88	0.010	17.44	2.03
120	116.4	0.88	0.010	17.50	2.02
121	117.4	0.92	0.010	17.39	2.04
122	118.2	0.90	0.010	17.27	2.04
123	119.0	1.01	0.010	17.22	2.05
124	120.0	0.96	0.010	17.26	2.05
125	121.0	0.93	0.010	17.27	2.07
126	122.0	0.91	0.010	17.45	2.07
127	122.8	0.93	0.010	17.32	2.06
128	123.6	0.89	0.010	17.47	2.07
129	124.6	0.91	0.010	17.18	2.11
130	125.5	0.87	0.010	16.80	2.18
131	126.4	0.95	0.010	16.56	2.19
132	127.6	1.07	0.010	15.81	2.30
133	129.0	1.32	0.010	15.60	2.38
134	130.0	1.31	0.010	15.60	2.42
135	130.9	1.16	0.010	15.63	2.40
136	131.8	1.20	0.010	15.58	2.43
137	132.8	1.41	0.010	15.55	2.53
138	133.6	1.34	0.010	15.28	2.51
139	134.4	1.33	0.010	15.49	2.52
140	135.4	1.29	0.010	15.50	2.53
141	136.3	1.28	0.010	15.34	2.54

CEB Cycle	Filtration Runtime (days)	Feed Turbidity (NTU)	Filtrate Turbidity (NTU)	Temperature (°C)	TMP (psi)
142	137.1	1.91	0.012	13.46	2.54
143	137.8	3.09	0.012	12.25	2.82
144	138.4	6.25	0.012	9.55	3.01
145	138.8	6.55	0.012	9.05	2.86
146	139.1	8.70	0.012	8.30	3.04
147	139.5	2.43	0.012	8.58	2.72
148	140.1	1.87	0.012	6.77	2.91
149	141.1	1.37	0.012	7.34	3.06
150	142.1	1.32	0.012	7.68	3.14
151	143.1	1.35	0.012	8.17	3.18
152	143.9	1.31	0.012	7.81	3.25
153	144.7	1.03	0.012	8.35	3.20
154	145.4	1.10	0.012	8.56	3.18
155	145.7	2.13	0.013	10.31	3.38
156	146.1	3.16	0.012	9.31	4.86
157	146.9	2.82	0.012	9.76	4.55
158	147.6	2.45	0.012	10.24	4.59
159	148.4	2.39	0.012	10.26	4.74
160	149.1	2.69	0.012	10.40	4.85
161	149.9	2.87	0.012	10.52	5.09
162	150.3	2.88	0.012	10.92	4.91
163	150.7	4.20	0.012	10.61	5.05
164	151.5	4.37	0.012	10.50	5.11
165	152.5	2.74	0.012	10.17	5.26
166	153.5	2.58	0.012	9.92	5.39
167	154.5	3.04	0.012	9.75	5.51
168	155.4	2.86	0.012	9.77	5.56
169	156.4	2.51	0.012	9.72	5.69
170	157.4	2.84	0.012	9.99	5.75
176	163.0	3.92	0.012	11.49	4.04
177	163.1	4.22	0.012	11.02	3.73
178	163.2	3.92	0.012	11.30	3.29
179	163.2	3.35	0.013	11.20	3.40
180	163.7	3.49	0.012	10.63	3.70
181	164.6	2.15	0.012	10.96	3.65
182	165.6	2.18	0.012	11.02	3.71

CEB Cycle	Filtration Runtime (days)	Feed Turbidity (NTU)	Filtrate Turbidity (NTU)	Temperature (°C)	TMP (psi)
183	166.5	1.65	0.012	11.57	3.70
184	167.5	1.47	0.012	11.85	3.70
185	168.4	1.13	0.011	12.72	3.71
186	169.4	4.07	0.012	12.99	5.66
187	170.3	2.48	0.012	13.32	5.13
188	171.2	2.20	0.012	13.07	4.75
189	172.2	2.32	0.012	13.07	4.59
190	173.2	1.98	0.012	12.44	4.60
191	174.0	2.09	0.012	12.08	4.39
192	174.8	2.10	0.010	13.21	4.45
193	175.8	2.09	0.010	13.15	4.46
194	176.8	2.12	0.011	13.35	4.42
195	177.8	1.93	0.012	13.69	4.35
196	178.8	2.18	0.012	14.35	4.26
197	179.8	1.85	0.012	12.26	4.58
198	180.5	1.55	0.012	10.88	4.83
199	181.2	1.30	0.012	9.95	5.15
200	181.8	1.40	0.012	10.16	5.02
201	182.3	1.95	0.012	11.39	5.13
202	183.3	1.87	0.012	15.55	4.59
203	184.3	1.94	0.012	16.03	4.47
204	185.3	1.41	0.012	15.80	4.46
205	186.0	1.25	0.012	16.06	4.38
206	186.2	1.00	0.012	15.90	4.03
207	186.7	1.50	0.012	15.01	4.56
208	187.7	1.87	0.012	14.75	4.62
209	188.7	1.53	0.012	14.89	4.69
210	189.7	1.62	0.012	15.01	4.75
211	190.5	1.62	0.012	15.38	4.67
212	191.2	1.70	0.012	15.35	4.82
213	192.1	1.79	0.012	16.26	4.70
214	192.6	1.60	0.012	16.75	4.35
215	193.1	1.39	0.010	17.33	4.49
216	194.1	1.46	0.010	17.48	4.55
217	195.1	1.56	0.010	17.66	4.60
218	196.1	1.56	0.010	17.76	4.49

CEB Cycle	Filtration Runtime (days)	Feed Turbidity (NTU)	Filtrate Turbidity (NTU)	Temperature (°C)	TMP (psi)
219	196.8	1.31	0.010	17.61	4.51
220	197.5	1.23	0.010	18.17	4.76
221	198.4	1.30	0.010	18.31	4.79
222	199.3	1.38	0.010	17.98	4.86
223	200.3	1.55	0.010	17.64	5.04
224	201.3	2.00	0.010	17.27	5.30
225	202.3	2.37	0.012	16.78	5.68
226	202.8	0.40	0.015	17.74	4.93
227	203.2	2.85	0.012	16.49	5.35
228	204.1	3.00	0.012	16.34	5.48
229	205.0	2.05	0.012	16.80	5.54
230	206.0	2.58	0.012	16.61	5.80
231	207.0	2.36	0.012	16.37	6.00
232	208.0	2.12	0.012	15.93	6.25
233	208.6	2.55	0.012	15.46	5.93
248	219.8	1.41	0.010	19.96	3.96
249	220.4	1.19	0.010	20.48	3.95
250	221.2	0.95	0.010	19.17	4.10
251	222.0	0.85	0.010	17.97	4.43
252	222.8	0.92	0.010	17.98	4.70
253	223.8	1.06	0.010	17.86	4.88
254	224.8	1.14	0.010	19.11	4.79
255	225.8	1.23	0.010	20.18	4.56
256	226.8	1.25	0.010	20.51	4.32
257	227.8	1.31	0.010	20.48	4.24
258	228.8	1.31	0.010	19.75	4.29
259	229.5	1.22	0.010	19.01	4.29
260	230.2	1.54	0.010	18.48	4.44
261	231.2	1.91	0.010	17.87	4.55
262	232.2	2.12	0.010	17.78	4.63
263	233.0	2.29	0.010	18.32	4.58
264	233.5	0.98	0.010	18.31	4.47
265	234.1	1.64	0.010	18.58	4.68
266	235.1	1.75	0.010	17.73	4.91
267	236.1	2.08	0.010	17.72	5.03
268	237.1	2.46	0.010	17.60	5.04

CEB Cycle	Filtration Runtime (days)	Feed Turbidity (NTU)	Filtrate Turbidity (NTU)	Temperature (°C)	TMP (psi)
269	237.7	2.48	0.010	17.41	4.89
270	238.3	1.27	0.010	16.95	5.27
271	239.3	1.46	0.010	16.92	5.51
272	240.3	1.46	0.010	16.59	5.81
273	241.3	1.74	0.010	17.40	5.84
274	242.2	1.99	0.010	17.64	6.09
275	242.7	1.88	0.010	17.36	5.98
276	243.3	2.09	0.010	17.96	6.11
277	244.3	1.87	0.010	19.05	6.07
278	245.3	2.11	0.010	19.96	6.08
279	246.3	2.69	0.010	20.70	5.89
280	247.0	2.37	0.010	20.77	5.69
317	275.9	0.70	0.010	23.98	1.90
318	276.8	0.73	0.010	23.75	1.90
319	277.8	0.73	0.010	23.62	1.92
320	278.8	0.67	0.010	23.32	1.94
321	279.8	0.72	0.010	23.30	1.96
322	280.8	0.83	0.010	23.23	1.97
323	281.7	0.65	0.010	23.06	1.96
324	282.5	0.76	0.010	23.12	1.98
325	283.4	0.94	0.010	22.48	2.08
326	284.4	0.97	0.010	21.64	2.13
327	285.2	1.06	0.010	21.52	2.08
328	285.7	1.26	0.010	21.02	2.14
329	286.3	0.82	0.010	21.61	2.14
424	360.6	1.11	0.010	14.98	2.40
425	361.0	0.99	0.010	14.79	2.18
428	361.6	1.29	0.013	8.91	2.58
429	362.5	1.13	0.013	8.39	3.06
430	363.0	1.28	0.013	8.24	3.06
431	363.6	1.00	0.013	8.71	3.13
432	364.6	1.90	0.013	9.07	3.27
433	365.4	2.59	0.013	8.83	3.32
435	366.1	2.02	0.013	8.54	3.13
436	366.8	1.47	0.012	8.33	3.33
437	367.6	1.65	0.012	8.41	3.46

CEB Cycle	Filtration Runtime (days)	Feed Turbidity (NTU)	Filtrate Turbidity (NTU)	Temperature (°C)	TMP (psi)
438	368.7	1.28	0.012	8.54	3.67
439	369.9	1.29	0.013	8.72	3.74
440	370.6	1.50	0.013	8.96	3.76
441	371.4	1.59	0.013	8.81	3.83
442	372.1	1.29	0.013	8.63	3.86
443	372.9	1.27	0.013	8.76	3.93
444	373.5	1.58	0.013	9.05	3.90
446	374.1	1.87	0.013	9.06	3.65
447	374.8	1.80	0.013	9.14	3.79
448	375.3	1.88	0.013	9.19	3.73
449	375.5	1.63	0.003	9.53	3.65
450	375.6	2.48	0.010	12.70	2.53
451	376.1	1.47	0.010	10.29	3.42
452	377.1	1.33	0.010	10.31	3.67
453	377.9	1.48	0.010	10.47	3.74
454	378.7	1.45	0.010	10.69	3.73
455	379.7	0.90	0.010	11.40	3.51
456	380.7	0.85	0.010	11.51	3.46
457	381.9	1.00	0.010	11.34	3.60
458	383.2	0.98	0.010	10.77	3.76
459	384.2	1.00	0.010	10.44	3.75
460	384.7	0.87	0.010	10.90	3.39
461	385.2	0.93	0.010	10.72	3.52
462	386.2	1.14	0.010	10.46	3.53
463	387.0	1.24	0.010	10.46	3.49
464	387.5	1.31	0.010	10.36	3.49
465	388.2	1.28	0.010	10.54	3.52
466	389.2	1.32	0.010	10.92	3.51
467	390.2	1.19	0.010	11.17	3.47
468	391.2	1.24	0.010	11.17	3.61
469	392.2	1.31	0.010	11.29	3.70
470	393.2	1.41	0.010	11.73	3.72
471	394.2	1.43	0.010	12.58	3.79
472	395.2	1.41	0.010	12.78	3.81
473	396.1	1.57	0.010	12.79	3.81
474	397.1	1.39	0.010	13.06	3.71

CEB Cycle	Filtration Runtime (days)	Feed Turbidity (NTU)	Filtrate Turbidity (NTU)	Temperature (°C)	TMP (psi)
475	397.7	2.14	0.010	12.13	3.73
476	398.2	1.64	0.010	13.25	3.50
477	399.1	1.42	0.010	13.70	3.38
478	400.1	1.46	0.010	13.52	3.40
479	400.9	1.36	0.010	13.75	3.35
479	401.4	1.27	0.010	14.21	3.31
480	402.1	1.62	0.010	14.40	3.32
481	403.1	1.30	0.010	14.33	3.31
482	403.8	1.17	0.010	13.95	3.29
483	403.9	0.95	0.010	14.40	2.67
484	404.4	1.00	0.010	14.26	3.18
485	405.4	1.23	0.010	14.05	3.18
486	406.4	1.18	0.010	14.00	3.18
487	407.3	1.34	0.010	13.59	3.20
488	408.2	0.95	0.010	13.37	3.17
489	409.2	0.90	0.010	13.91	3.22
490	410.1	1.34	0.010	14.24	3.26
491	411.1	0.95	0.010	14.49	3.23
492	412.1	0.96	0.010	14.88	3.23
493	413.1	1.34	0.010	15.45	3.25
494	414.0	1.78	0.010	15.74	3.32
495	414.7	1.75	0.010	15.76	3.23
496	415.3	1.78	0.009	15.46	3.20
497	416.3	1.93	0.009	15.45	3.28
498	417.3	1.77	0.009	15.19	3.32
499	418.3	1.52	0.009	15.54	3.28
500	419.3	1.37	0.009	16.07	3.25
501	420.2	1.35	0.009	16.20	3.24
502	421.1	1.25	0.009	15.92	3.25
503	422.1	0.91	0.009	15.98	3.30
504	423.1	1.08	0.009	16.18	3.39
505	424.1	1.19	0.009	16.04	3.36
506	425.1	1.42	0.009	16.39	3.41
507	426.1	1.25	0.009	16.45	3.33
508	426.6	1.28	0.009	17.49	2.98
508	427.0	1.84	0.009	16.78	3.30

CEB Cycle	Filtration Runtime (days)	Feed Turbidity (NTU)	Filtrate Turbidity (NTU)	Temperature (°C)	TMP (psi)
509	427.7	1.38	0.009	15.80	3.34
510	428.5	1.16	0.009	15.50	3.40
511	429.5	1.02	0.009	16.06	3.37
512	430.5	1.01	0.009	16.33	3.43
513	431.5	1.10	0.009	15.53	3.32
514	432.4	1.05	0.009	15.22	3.26
515	433.4	1.10	0.008	14.25	3.31
516	434.4	1.12	0.008	14.47	3.26
517	435.4	1.00	0.008	15.07	3.25
518	436.4	0.83	0.008	14.51	3.26
519	437.4	0.73	0.008	15.08	3.18
520	438.4	0.64	0.008	15.57	3.07
521	439.3	0.66	0.008	16.70	2.97
522	440.3	0.58	0.008	17.86	2.91
523	441.3	0.47	0.008	18.04	2.79
524	442.3	0.78	0.008	18.13	2.93
525	443.3	1.18	0.009	17.87	2.95
526	444.3	0.97	0.009	17.68	2.91
527	445.3	0.78	0.009	17.23	2.89
528	446.2	0.68	0.009	18.56	2.80
529	447.0	0.83	0.010	17.94	2.72
530	447.8	1.03	0.009	18.64	2.70
531	448.8	1.02	0.009	18.54	2.86
532	449.8	0.90	0.009	18.19	2.89
533	450.7	0.97	0.009	17.98	2.84
534	451.6	1.16	0.009	18.27	2.79
535	452.6	1.72	0.008	17.21	2.90
536	453.5	1.82	0.008	17.12	2.86
537	454.4	1.30	0.007	17.52	2.75
538	455.4	1.19	0.008	16.48	2.77
539	456.4	1.00	0.008	16.41	2.73
540	457.2	1.42	0.008	16.80	2.66
541	457.6	1.39	0.008	18.27	2.39
542	458.9	1.17	0.008	18.35	2.52
543	459.8	0.97	0.008	19.21	2.46
544	460.8	0.76	0.008	19.91	2.37

CEB Cycle	Filtration Runtime (days)	Feed Turbidity (NTU)	Filtrate Turbidity (NTU)	Temperature (°C)	TMP (psi)
545	461.8	0.55	0.008	19.53	2.39
546	462.8	0.49	0.008	18.80	2.51
547	463.7	0.61	0.008	18.29	2.55
548	464.5	1.04	0.008	17.85	2.46
549	465.3	0.90	0.008	18.25	2.37
550	466.3	0.60	0.008	18.03	2.44
551	467.3	0.58	0.008	17.82	2.50
552	468.3	0.57	0.008	17.81	2.51
553	469.3	0.53	0.008	17.78	2.52
554	470.3	0.53	0.008	18.29	2.47
555	471.2	0.54	0.008	19.30	2.41
556	472.2	0.41	0.008	16.48	2.49
557	473.2	0.43	0.008	16.47	2.50
558	474.2	0.43	0.008	16.08	2.53
559	475.1	0.68	0.008	17.27	2.56
560	476.1	0.82	0.008	18.00	2.54
561	477.0	1.14	0.009	18.02	2.50
562	477.8	0.91	0.010	18.56	2.48
563	478.2	0.78	0.011	19.09	2.31