

PHYSICAL-CHEMICAL TREATMENT OF GROUNDWATER AND MEMBRANE
CONCENTRATE TO DECREASE MEMBRANE FOULING POTENTIAL

By

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To my parents

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LIST OF ABBREVIATIONS

Ca ²⁺	Calcium
CaO	Calcium Oxide
DI	Deionized
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EEM	Excitation-emission matrix
ERD	Effective resin dose
GWTP	Groundwater treatment plant
MIEX-Cl	Magnetic ion exchange resin in chloride form
NaCl	Sodium chloride
NF	Nanofiltration
NOM	Natural organic matter
RO	Reverse osmosis
SO ₄ ²⁻	Sulfate
SUVA ₂₅₄	Specific ultraviolet absorbance at 254 nm
TDS	Total dissolved solids
UV ₂₅₄	Ultraviolet absorbance at 254 nm

Abstract of Thesis Presented to the Graduate School
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The overall objective of this work is to evaluate physical-chemical treatment of groundwater and membrane concentrate to reduce the membrane fouling potential of these waters. Anion, cation, and combined ion exchange were studied for pretreatment of groundwater for high-pressure membrane filtration. Coagulation, softening, and anion exchange were studied for treatment of membrane concentrate. To determine the efficiency of these treatment processes, the membrane fouling potential was calculated. The membrane fouling potentials were defined as: inorganic fouling potential = $(Ca^{2+}[SO_4^{2-}])/([Ca^{2+}]_0[SO_4^{2-}]_0)$ and organic fouling potential = $[DOC]/[DOC]_0$, where the subscript 0 indicates initial concentration. By removing dissolved organic matter and total dissolved solids from both types of water, membrane fouling can be reduced which results in higher recovery rates.

To evaluate combined ion exchange pretreatment, three different groundwaters with high dissolved organic matter and total hardness were collected for evaluation. Preliminary experiments were performed with anion and cation exchange resins. Additionally, single-use and multiple loading jar test procedures were studied to determine differences in performance. Combined ion exchange was found to be

effective for reducing both inorganic and organic fouling potentials of groundwater, while producing only one waste stream. In order to reduce membrane fouling potential of membrane concentrate, three established drinking water treatment processes were evaluated. Although coagulation, softening, and anion exchange were able to reduce either inorganic or organic fouling, a treatment process that removes both types of membrane fouling is necessary in order to have an effective treatment process. Thus, combined treatment processes including combined ion exchange are promising pretreatment methods for high-pressure membrane filtration.

This work provides an improved understanding of physical-chemical treatment processes that reduce membrane fouling. Increasing knowledge of the entire high-pressure membrane filtration system, from pretreatment to management of residuals, is imperative as alternative sources of water are increasingly integrated into water treatment. Overall, this work demonstrates that established drinking water treatment processes can be applied to concentrated waste streams and that combined ion exchange is a promising treatment technology for reducing membrane fouling.

CHAPTER 1 INTRODUCTION

Global populations and agricultural activity are expected to increase significantly over the next few decades, which will increase water demand. This trend is very prominent in Florida where the population is expected to increase to 25.9 million people by 2025 (U.S. Census Bureau, 2004), resulting in a 2 billion gallons per day increase in water demand (FDEP, 2007). The projected increased water demand has prompted the water management districts in Florida to turn to alternative sources of water including surface water, brackish water, seawater, and reclaimed water. Along with better use of these naturally occurring sources of water, the water management districts plan to incorporate management techniques including water resource development, demand management, and use of reclaimed water in order to meet the future water needs for the state of Florida (SJRWMD, 2006).

Alternative sources of water are more difficult to treat compared to existing water sources due to a higher concentration of natural organic matter (NOM), total dissolved solids (TDS), and possible organic compounds from pesticides, fertilizers, and pharmaceuticals. Thus, more advanced water treatment processes are needed to adequately clean the alternative sources. High-pressure membrane processes are common water treatment processes used to remove TDS and dissolved organic matter (DOM). However, there are two main obstacles to overcome when implementing membrane filtration processes: i) fouling of the membrane units due to DOM and TDS and ii) disposal of membrane concentrate which is the by-product of membrane filtration. Although membrane filtration produces high quality finished water, these obstacles may prevent utilities from investing in membrane technology. Additionally as

water treatment plants increasingly integrate alternative water sources into their raw water source, membrane processes will become even more prevalent. Thus, the issues of membrane fouling and membrane concentrate disposal need to be better studied.

To decrease the membrane fouling issues encountered in membrane filtration, source water typically goes through several pretreatment steps. Common pretreatment processes may include ultrafiltration, microfiltration, anti-scalant addition, and pH adjustment (Greenlee et al., 2009). However, despite the pretreatment processes membrane fouling still occurs, and it would be expected that as water treatment plants shift toward alternative water sources, more intensive pretreatment processes would be necessary to remove additional scaling components from these lower quality water sources. Ion exchange is an established water treatment process that is beginning to be studied for membrane filtration pretreatment (Cornelissen et al., 2010; Heijman et al., 2009). Cornelissen et al. (2010) studied anion exchange to reduce membrane fouling, while Heijman et al. (2009) studied cation exchange as a step to achieve zero liquid discharge. However combined ion exchange, which involves anion and cation exchange conducted in the same reactor, has not yet been well studied as a pretreatment or water treatment process. Combined ion exchange is advantageous because it can remove both organic and inorganic constituents (Apell and Boyer, 2010). Additionally combined ion exchange uses the regenerant brine more efficiently.

Membrane concentrate is a high ionic strength wastewater produced as a by-product of membrane filtration. Common disposal methods of membrane concentrate include discharge to a wastewater treatment plant, discharge to a surface water body, deep-well injection, and ocean-outfall. Water scarcity is widespread and will continue to

increase in severity; water effluent quality standards are becoming increasingly stringent, and thus, membrane concentrate needs to be better understood as more treatment plants establish high-pressure membrane filtration processes. Removing fouling components from membrane concentrate prior to sending it through a membrane unit can improve the overall recovery rate at a treatment plant, ultimately decreasing the total volume of wastewater. Additionally, membrane concentrate treatment may be needed prior to disposal so as to not alter natural ecosystems or biological processes at wastewater treatment plants.

Membrane treatment processes are likely to become more prevalent as alternative sources of water are utilized. Thus, pretreatment and post-treatment aspects of membrane filtration need to be better understood. The title of Chapter 2 is “Combined Ion Exchange as Pretreatment for High-Pressure Membrane Processes.” Chapter 2 will discuss combined ion exchange treatment of groundwater with high hardness and DOM. Additionally, variations in jar testing procedures were assessed to estimate reproducibility and full-scale efficiency. The title of Chapter 3 is “Effect of Membrane Concentrate Chemistry on Coagulation, Softening, and Anion Exchange Treatability.” Chapter 3 is a systematic study of physical-chemical treatment of membrane concentrate. Major findings from Chapters 2 and 3 are presented in Chapter 4, along with suggestions for future work.

CHAPTER 2 COMBINED ION EXCHANGE AS PRETREATMENT FOR HIGH-PRESSURE MEMBRANE PROCESSES

2.1. Combined Ion Exchange Pretreatment Overview

Water utilities need to adapt their water treatment processes in order to accommodate changing water quality and alternative sources of water. In areas where surface water is used for drinking water, groundwater resources may help augment diminishing surface water bodies and vice versa. Depending on the type of permeable rock that contains the aquifer, groundwater that is extracted from this aquifer may contain high concentrations of calcium, magnesium, and other divalent cations that constitute the hardness of the water. Additionally shallow aquifers may be considered as “under the influence of surface water”, and thus, the groundwater may have a high organic matter concentration. As over-pumping of groundwater continues, saltwater intrusion will become more prevalent in coastal regions. All of these scenarios result in source water that is more difficult to treat. Thus, the water treatment processes may need to be modified to accommodate alternative sources of water or changing water quality.

For membrane processes to be a feasible option for treating alternative sources of water, efficient pretreatment processes are necessary. Pretreatment processes are also important because they affect the characteristics of the permeate and concentrate (Squire, 2000; Van der Bruggen et al., 2003). Common pretreatment processes include microfiltration, anti-scalant addition, and pH adjustment (Greenlee et al., 2009). Other membrane pretreatment processes include coagulation (Baek and Chang, 2009; Choi and Dempsey, 2004), anion exchange (Cornelissen et al., 2010), and cation exchange (Heijman et al., 2009). These treatment processes typically target either organic (i.e.

DOM, organic compounds such as pesticides and endocrine disrupting compounds) or inorganic (i.e. divalent cations, total dissolved solids) constituents. Coagulation targets removal of organic constituents of source water. Baek and Chang, (2009) studied the effect of coagulation with ferric sulfate and alum prior to ultrafiltration of wastewater treatment plant effluent. They found that coagulation was effective for reducing membrane fouling, and that coagulation pretreatment was more beneficial for hydrophobic membranes. Also, Choi and Dempsey, (2004) found that in-line alum coagulation reduced fouling of ultrafiltration membranes. Cornelissen et al. (2010) studied the effect of fluidized anion exchange to reduce membrane fouling due to NOM. They found that removing NOM did not reduce membrane fouling because the humic substances removed by anion exchange did not adsorb to the membrane surface. Heijman et al. (2009) found that cation exchange as pretreatment of surface water prior to ultrafiltration, nanofiltration, and activated carbon filtration could achieve 97% recovery.

These various pretreatment processes have been shown to be effective for removing either organic or inorganic foulants. However, alternative water sources will likely have both organic and inorganic components that need to be removed prior to membrane filtration. Thus, combining two or more pretreatment processes may be necessary to significantly reduce membrane fouling. For example anion exchange is becoming more prevalent for removal of sulfate, DOM and other negatively charged constituents, and cation exchange can be used for removal of ions that contribute to hardness. Thus, combined ion exchange should be investigated as a possible treatment option for water that is high in hardness and DOM. Combined ion exchange is not only

suitable for producing high quality drinking water, but it also produces water that has a lower membrane fouling potential which can improve recovery rates (Apell and Boyer, 2010). Combined ion exchange can occur within the same reactor, which allows for the most efficient use of the regenerant solution (Apell and Boyer, 2010). Additionally, combined ion exchange would produce only one waste stream, the regenerant brine. Traditionally, lime softening is used to remove hardness cations, which produces sludge; if DOM removal is necessary, anion exchange or coagulation may be used which produces either regenerant brine or sludge, respectively.

More advanced treatment technology will be necessary for water treatment as source water quality changes. The overall goal of this work is to study combined ion exchange as pretreatment for membrane filtration. The specific objectives of this work are: (i) to evaluate the efficiency of hardness removal by strong and weak acid cation exchange resins; (ii) to compare the efficiency of anion exchange resin for single use and for multiple loadings; and (iii) to evaluate the efficiency of combined ion exchange treatment in terms of hardness and DOM removal.

2.2. Experimental

2.2.1. Sources of Groundwater

All groundwater samples examined in this work were collected from well fields used by municipal water treatment plants in Florida, USA. All groundwater samples were collected using sampling ports on well pumps, transported to the laboratory on ice, stored at 4° C, and tested within 3 months of collection. Groundwater was collected from 3 different sites: GWTP-1, GWTP-2, and GWTP-3. Groundwater was collected from all water treatment plants once in September 2010, and GWTP-1 was collected again in January 2011.

2.2.2. Ion Exchange Resins

Three ion exchange resins were examined in this work. For anion exchange experiments, a magnetic ion exchange resin manufactured by Orica Watercare was used with chloride as the mobile counter anion (MIEX-Cl). For cation exchange, Amberlite® 200C and Purolite® C107E were used with sodium as the mobile counter cation. Table 2-1 lists resin characteristics. All resins were dosed volumetrically using a graduated cylinder.

2.2.3. Treatment Chemicals

Sodium chloride (NaCl; Fisher Scientific; certified ACS) was used to clean and regenerate the resins. Standard chemicals used in analytical methods are described below. Deionized (DI) water was used to prepare all chemical reagents and standards. Glassware was cleaned with laboratory detergent, rinsed three times with DI water, and if necessary, soaked overnight in a 6% nitric acid solution.

2.2.4. Ion Exchange Jar Tests

2.2.4.1. Preliminary experiments

In order to evaluate the effectiveness of ion exchange resins for all groundwaters, preliminary experiments were performed with different doses of each resin. A Phipps & Bird PB-700 jar tester was used to conduct various jar test treatments. All ion exchange resins were measured as described in Apell and Boyer (2010). The amount of ion exchange resin in mL used to treat a certain amount of water in L will be referred to as the effective resin dose (ERD). For preliminary experiments, the effective resin doses were as follows: 1, 2, and 4 mL/L MIEX-Cl resin; 4, 8, and 12 mL/L Amberlite® 200C resin; and 2, 4, and 6 mL/L Purolite® C107E resin. Amberlite® 200C resin doses were chosen based on preliminary data from (Apell and Boyer, 2010), and Purolite® C107E

resin doses were chosen to have a similar total capacity as the Amberlite® 200C doses. Virgin anion exchange resin was cleaned prior to use based on Apell and Boyer (2010), except the resin was mixed in the salt solution for 10 min at 100 rpm, and then rinsed in DI water for 10 min at 100 rpm using the jar tester described above. Cation resins were cleaned similarly to the anion resin, except a 200 rpm mixing speed was used to ensure that the resin was dispersed evenly. The cleaned virgin resin is referred to as fresh resin. All experiments were performed with fresh resin. The same cleaning procedure was followed to regenerate used resin. The used resin that has been regenerated is referred to as regenerated resin. The preliminary anion exchange procedure was as follows: mix at 100 rpm for 30 min and settle for 5 min. Again, the cation exchange procedure was similar to that of anion exchange except a 200 rpm mixing speed was used. Samples were collected at 5, 10, 20, and 30 min (after settling). All samples were removed directly from the jar using a syringe fitted with a PVDF 0.45 μm filter (Millex-HV, Millipore) and analyzed for ultraviolet (UV) absorbance at 245 nm (UV_{254}) and/or total hardness.

2.2.4.2. Multiple loading experiments

Multiple loading experiments were performed with MIEX-Cl and/or Amberlite® 200C in order to better simulate the resin efficiency in a full-scale scenario. Fresh resin described above was used for multiple loading experiments. The resin doses used for multiple loading experiments were determined by multiplying the effective resin dose from the preliminary results by the total number of liters of water to be treated. This resin dose is referred to as the multiple loading dose, and it is equivalent to an effective resin dose used in preliminary experiments. The fresh resin was added to 1 L of GWTP-

1 water, and the ion exchange jar test procedure was followed as described above. After 30 min of mixing and 5 min of settling, a 150 mL sample was taken for analysis. Additionally, a 50 mL sample was taken by volumetric pipette for a composite sample. After sampling, the treated water was decanted and 1 L of untreated source water was added to the used resin. The same mixing and sampling procedures were followed. These steps were repeated until 5 L of water were treated by the ion exchange resin. In order to determine if the single-use and multiple loading procedures using the same effective resin dose were equivalent, data from a multiple loading experiment using 5 mL/L MIEX-CI that treated five 1-L batches of GWTP-1 was compared to data for GWTP-1 collected in the preliminary experiments with an effective resin dose of 1 mL/L MIEX-CI. Based on these results, the multiple loading procedure was used for all combined ion exchange experiments.

2.2.4.3. Combined ion exchange experiments

MIEX-CI and Amberlite® 200C were chosen for combined ion exchange experiments based on preliminary results. All combined ion exchange experiments followed the multiple loading procedure to better predict resin performance at the full-scale. Because MIEX-CI and Amberlite® 200C have different exchange site capacities, the resin was regenerated at a 10 times sodium chloride concentration in relation to the capacity of Amberlite® 200C. Thus, MIEX-CI was regenerated at a level much higher than 10 times the resin capacity. The multiple loading resin doses used were 5 mL/L MIEX-CI and 20 mL/L Amberlite® 200C. The multiple loading jar tests for combined ion exchange were followed as described above, except a 200 rpm mixing speed was used ensure that the more dense Amberlite® 200C resin was evenly dispersed. Again, 5 L of

water was treated and the composite sample comprised of equal volume of treated water from each loading cycle. Thus, the effective resin doses for combined ion exchange experiments were 1 mL/L MIEX-CI and 4 mL/L Amberlite® 200C.

2.2.5. Analytical Methods

Raw groundwater samples were analyzed for pH, UV₂₅₄, DOC, sulfate, total hardness, calcium hardness, and alkalinity. Samples from preliminary anion exchange experiments were analyzed for UV₂₅₄. Samples from preliminary cation exchange experiments were analyzed for UV₂₅₄ and total hardness. Samples from the GWTP-1 multiple loading experiment were analyzed for pH, UV₂₅₄, DOC, and sulfate. Combined ion exchange samples were analyzed for pH, UV₂₅₄, DOC, sulfate, total hardness, and alkalinity. Samples not collected with a syringe fitted with a PVDF 0.45 μm filter (Millex-HV, Millipore) were filtered through 0.45 μm nylon membrane filters (Millipore). pH, DOC, and UV₂₅₄ were analyzed as described in Comstock et al. (2010).

Total hardness was determined following Standard Methods 2340 (Clesceri et al., 1989). Reagents were made according to Standard Methods 2340. Calmagite was used as the indicator. Calcium hardness was determined following Standard Methods 3500-Ca D. However instead of using a 0.2% Eriochrome Blue Black R indicator, a 0.5% Eriochrome Blue Black R indicator was used to make the color change more noticeable. Alkalinity was determined by following Standard Methods 2320. Standard 0.02 N sulfuric acid was used as the titrant and bromcresol green was used as the indicator. For all titrations, once the end point was reached, this value was recorded and a few more drops of titrant were added to ensure that the color change was complete. SO₄²⁻ was measured by ion chromatography as described in Apell and Boyer (2010).

2.3. Results and Discussion

2.3.1. Raw Water Characteristics

Groundwaters with high concentrations of hardness and DOM were used for all experiments. Table 2-2 provides water quality information for the untreated groundwaters. GWTP-1 and GWTP-3 have high DOC concentrations of 6.5 mg/L and 9.8 mg/L, respectively. GWTP-2 has a high sulfate concentration of 134 mg/L, which will lead to competition between sulfate and DOM for resin exchange sites. All source waters have high specific ultraviolet absorbance at 254nm ($SUVA_{254}$), indicating that the DOM in these waters is more aromatic than aliphatic (Weishaar et al., 2003). According to previous research, DOM removal by anion exchange will be more effective in waters with $SUVA_{254} > 3$ L/mg C·m and sulfate < 50 mg/L (Boyer and Singer, 2005, 2006). Thus, based on Table 2-2 better DOM removal can be expected for GWTP-1 and GWTP-3. All waters have high hardness, the majority of which is associated with calcium. This is beneficial because cation exchange resins typically have a higher affinity for calcium rather than magnesium (Helfferich, 1995). All treatment plants that use these source waters utilize MIEX-Cl resin for DOM removal and softening for hardness removal. Because these source waters contain both high hardness and DOC, substantial treatment is required in order to prevent problems associated with elevated concentrations of hardness and DOC, such as formation of disinfection byproducts and membrane fouling.

2.3.2. Organic and Inorganic Removal by Ion Exchange Resins

Preliminary jar tests were performed with either anion or cation exchange resin. Various doses and performance at various mixing times were monitored to evaluate the relationship between organic and inorganic constituent removal and resin dose, as a

function of time. Figure 2-1 shows UV_{254} removal for waters treated with MIEX-CI resin. All three waters follow a similar trend, however removal percentages vary. The highest resin dose at a final time of 30 min achieved the maximum removal for all waters. GWTP-1 had a maximum UV_{254} removal of 74%. High UV_{254} removal was expected due to the high $SUVA_{254}$ of GWTP-1 water. Sulfate was likely also removed because MIEX-CI has a high affinity for sulfate (Boyer and Singer, 2006), however sulfate was not measured during preliminary tests. GWTP-2 had a maximum UV_{254} removal of 77%. High UV_{254} removal was expected due to the high $SUVA_{254}$. Most likely sulfate also had high removal because GWTP-2 has such a high sulfate concentration of 134 mg/L. GWTP-3 had the best removal overall at 92% UV_{254} removal. GWTP-3 has a high aromatic carbon concentration as indicated by the high $SUVA_{254}$ value and the lowest sulfate concentration, both of which are advantageous for DOM removal by anion exchange. The kinetic portion of the data in Figure 2-1, as well as Figures 2-2 and 2-3, illustrate that similar levels of removal can be achieved at a low dose/long contact time and a high dose/short contact time. For example, 55% UV_{254} removal can be achieved for GWTP-1 at a dose of 1 mL/L MIEX-CI for 30 min, a dose of 2 mL/L MIEX-CI for 20 min, and a dose of 4 mL/L MIEX-CI for 5 min. Thus, once a desired level of DOM removal is determined, a cost-benefit analysis should be done for different combinations of resin dose and contact time to achieve this DOM removal.

To determine the efficiency of cation exchange, total hardness and UV_{254} were measured for water treated by Amberlite® 200C and Purolite® C107E. Figure 2-2 shows total hardness removal for waters treated by Amberlite® 200C. The highest resin dose at a final time of 30 min achieved the maximum total hardness removal. However,

the difference in removals at 30 min between the 8 mL/L and 12 mL/L Amberlite® 200C was < 4%. GWTP-1 had a maximum removal of 98% at a dose of 12mL/L Amberlite® 200C. Previous research has reported that GWTP-1 has an effluent hardness concentration of 170 mg/L as CaCO₃. In order to achieve the same amount of hardness removal, a dose of 4 mL/L Amberlite® 200C and a mixing time of 10 min or a dose of 8 mL/L and a mixing time of 5 min is required. GWTP-2 had a maximum total hardness removal of 99% at a dose of 12 mL/L Amberlite® 200C. In order to achieve hardness removal similar to GWTP-1 effluent, a dose of 4 mL/L Amberlite® 200C at a mixing time of 20 min or a dose of 8 mL/L at a mixing time of 10 min would be required. GWTP-3 had a maximum total hardness removal of 98% at a dose of 12 mL/L Amberlite® 200C. GWTP-3 had an initial total hardness concentration similar to that of GWTP-1, and thus, the same doses and mixing times would be required to achieve an effluent concentration ≤ 170 mg/L as CaCO₃. Amberlite® 200C had a much faster exchange rate compared to MIEX-Cl resin. UV₂₅₄ was measured for GWTP-2 and GWTP-3 treated by cation exchange resins, and no UV₂₅₄ removal was observed (results not shown).

Figure 2-3 shows total hardness removal for waters treated by Purolite® C107E. In general, total hardness removal was less with Purolite® C107E compared to Amberlite® 200C. Additionally the rate of exchange was slower for Purolite® C107E than Amberlite® 200C. The main difference between these two resins is that Amberlite® 200C is a strong acid resin, and Purolite® C107E is a weak acid resin. GWTP-1 had a maximum total hardness removal of 75% at a dose of 6 mL/L Purolite® C107E. Although less resin is needed compared to Amberlite® 200C because Purolite® C107E has a much higher capacity, more sodium chloride is needed to produce a

regenerant solution that is the proper concentration. GWTP-2 had the highest initial total hardness concentration and a maximum total hardness removal of 48%. GWTP-3 had a maximum total hardness removal of 62%. Based on initial concentrations and maximum removals, ~200 mg/L as CaCO₃ was removed by Purolite® C107E for all waters.

2.3.3. Comparison of Single-use and Multiple Loadings

The preliminary jar test procedure was followed for anion exchange treatment of GWTP-1 with an effective resin dose of 1 mL/L MIEX-Cl a total of 6 times in order to determine the repeatability of the remaining experiments. The coefficient of variation, defined as the standard deviation, σ , divided by the mean, μ , for UV₂₅₄, DOC, and sulfate was 11%, 8%, and 5%, respectively. The multiple loading jar test procedure was followed for anion exchange treatment of GWTP-1 with a multiple loading dose of 5 mL/L MIEX-Cl used to treat 5 L of water (i.e. an effective resin dose of 1 mL/L MIEX-Cl). Both single-use and multiple loading experiments were conducted at the same contact time of 30 min. Averaged data from the single loading procedure was compared to data from the multiple loading procedure, as shown in Figure 2-4. Theoretically, the 1 mL/L MIEX-Cl single loading procedure should produce similar removals to the composite from the multiple loading procedure with an effective resin dose of 1 mL/L MIEX-Cl. However, when comparing the data in Figure 2-4, the multiple loading procedure produced higher removals for UV₂₅₄, DOC, and sulfate than the single loading procedure. The multiple loading procedure had 84% UV₂₅₄ removal for the composite, while the single loading only had an average UV₂₅₄ removal of 57%. It is proposed that the multiple loading procedure is a more realistic representation of the full-scale MIEX-Cl treatment process. Thus, previous research that follows the single loading method

may have underestimated the efficiency of MIEX-Cl treatment. Because of these findings, subsequent combined ion exchange jar tests were performed following the multiple loading method. Additionally, future work should investigate varying contact time to achieve better agreement between single-use and multiple loading procedures.

Figure 2-4 also illustrates the resin affinity for aromatic carbon. UV_{254} removal stays fairly constant throughout the 5 loading cycles with a standard deviation of 0.003, whereas DOC removal begins to increase through subsequent loading cycles with a standard deviation of 0.4. As the resin exchange sites are occupied by DOM, aromatic carbon is being removed at a constant rate. However, the DOC concentration of the treated water increases throughout the loading cycles, which indicates that less and less aliphatic carbon is being removed. Additionally, sulfate removal decreases throughout the loading cycles, indicating that aromatic carbon is preferentially removed compared to sulfate.

2.3.4. Combined Ion Exchange with Multiple Loading Procedure

All source waters were used for combined ion exchange experiments following the multiple loading method. 5 mL/L MIEX-Cl and 20 mL/L Amberlite® 200C were used for combined ion exchange, which is equivalent to an effective resin dose of 1 mL/L MIEX-Cl and 4 mL/L Amberlite® 200C. The MIEX-Cl resin dose was chosen based on preliminary results and the anion exchange multiple loading jar tests with GWTP-1. The Amberlite® 200C resin dose was chosen based on preliminary results where > 70% total hardness removal was achieved in all source waters with a dose of 4 mL/L. Figure 2-5 shows GWTP-1 water treated by combined ion exchange for a) 1st loading cycle after resin was cleaned and b) 2nd loading cycle after resin was regenerated. There are

some limitations of this data (i.e. fluctuations in the 1st loading and poor agreement between the 1st and 2nd loadings) because a different batch of GWTP-1 was integrated during the 1st loading cycle. Although both batches of GWTP-1 water were collected at the same time, it appears as though one batch had a higher DOM content and the other batch had a higher sulfate concentration. For the first loading cycle, the order of removal was: total hardness > DOC > UV₂₅₄ > sulfate ≈ alkalinity. The second loading cycle had an order of removal as follows: UV₂₅₄ > DOC > total hardness > sulfate > alkalinity. The cation resin capacity is reached sooner than that of the anion resin because the total hardness concentration is much higher than the DOM concentration. Lower total hardness removal during the 2nd loading cycle indicates that a 10× NaCl regenerant solution does not adequately clean the resin. Figure 2-6 shows GWTP-2 water treated by combined ion exchange for a) 1st loading cycle with fresh resin, and b) 2nd loading cycle with regenerated resin. For the 1st loading cycle, the order of removal was: UV₂₅₄ > total hardness > DOC > sulfate > alkalinity. The order of removal for the 2nd loading cycle was: UV₂₅₄ > DOC > total hardness > sulfate > alkalinity. DOM removal is fairly consistent throughout the first loading cycle. However, total hardness and sulfate removal decline as more source water is treated. Although the resin has a higher affinity for DOM than sulfate, approximately 20 mg/L of sulfate was removed during the 1st and 2nd loading cycles. Overall total hardness removal is only 40% in the 2nd loading cycle compared to 55% in the 1st loading cycle, which indicates that the 10× NaCl regenerant solution did not adequately clean the resin. Combined ion exchange had a minimal effect on alkalinity. Figure 2-7 shows GWTP-3 water treated by combined ion exchange for 2 loading cycles. The order of removal for the 1st loading cycle was: UV₂₅₄ > DOC ≈

total hardness > sulfate > alkalinity, and the order of removal for the 2nd loading cycle was: UV₂₅₄ > DOC > sulfate > total hardness > alkalinity. Similar trends observed for GWTP-2 pertain to GWTP-3. However, greater sulfate and total hardness removal is achieved because their initial concentrations are lower for GWTP-3 compared to GWTP-2. In general, DOM removal was fairly consistent during 2 multiple loading cycles of combined ion exchange. However compared to the 1st loading cycle, total hardness removal efficiency greatly decreased during the 2nd loading cycle. Thus, the anion exchange resin is being adequately cleaned by a 10× NaCl solution while the cation exchange resin is not.

Because Amberlite® 200C was not performing well during the 2nd loading cycle, a more concentrated regenerant solution was tested for GWTP-1. The resin was initially cleaned and regenerated after the 1st loading cycle in a 100× NaCl solution. These results are shown in Figure 2-8. The order of removal for the 1st loading cycle was: total hardness > DOC > UV₂₅₄ > sulfate > alkalinity. The composite had a total hardness removal of 99%. Again, DOM removal based on UV₂₅₄ and DOC was fairly consistent throughout the multiple loadings. However unlike the multiple loading experiments performed with a 10× NaCl regenerant solution, aromatic carbon removal was not preferentially removed compared to aliphatic carbon. It is not clear why this change occurred. The order of removal for the 2nd loading cycle was the same as the 1st loading cycle. Removals of all parameters in the 2nd loading cycle were consistent with removals from the 1st loading cycle except total hardness. The 2nd loading cycle composite had a total hardness removal of 96%. The removal efficiency only decreases from the 1st to

the 2nd loading cycles by 3% compared to 15-30% at a 10× NaCl regenerant solution, indicating that the 100× NaCl solution adequately cleaned the resin.

In terms of DOM and total hardness removal, combined ion exchange was effective for removing membrane fouling precursors. These results are fairly representative of full-scale performance because the multiple loading procedure better simulates the full-scale treatment process. In order to quantify the efficiency of combined ion exchange in terms of reducing membrane fouling, a theoretical membrane fouling potential was calculated based on work by Apell and Boyer, (2010). The membrane fouling potentials were defined as: inorganic fouling potential = $(Ca^{2+}][SO_4^{2-}]) / ([Ca^{2+}]_0[SO_4^{2-}]_0)$ and organic fouling potential = $[DOC] / [DOC]_0$, where the subscript 0 indicates initial concentration. Total hardness in mg/L as CaCO₃ was converted to mg/L as Ca²⁺ and used to calculate inorganic fouling potential. Figure 2-9 shows the theoretical membrane fouling potential associated with groundwater treated by combined ion exchange. Part a) of Figure 2-9 shows both inorganic and organic fouling potentials for both cycles of combined ion exchange treatment for all groundwaters at a resin regeneration level of 10× NaCl for 20 mL/L Amberlite® 200C. Membrane fouling potential was reduced by > 50% for all groundwaters. Combined ion exchange was most effective for reducing membrane fouling potential for GWTP-3, which had a high SUVA₂₅₄ and the lowest total hardness and sulfate concentrations. Organic fouling potential is less variable in terms of loading cycle when compared to inorganic fouling potential. Part b) of Figure 2-9 shows inorganic and organic fouling potentials for both cycles of combined ion exchange treatment of GWTP-1 at 10× and 100× NaCl for 20 mL/L Amberlite® 200C. Organic fouling potential was not affected by the strength of the

regenerant solution. However, inorganic fouling potential was greatly reduced with the use of a 100× NaCl regenerant solution.

2.4. Combined Ion Exchange Pretreatment Summary

This work provides a systematic study of combined ion exchange as a pretreatment process for membrane filtration. DOM and total hardness were specifically targeted for removal due to their propensity of fouling membrane units. The major findings are as follows:

The strong acid resin Amberlite® 200C was more effective for total hardness removal compared to the weak acid resin Purolite® C107E, even though Purolite® C107E has a total capacity 2× that of Amberlite® 200C. The difference in efficiency is likely due to the differences in resin structure. Amberlite® 200C has a macroporous, highly crosslinked structure allowing for ions to be held closely to the resin, while Purolite® C107E has a polyacrylic matrix structure.

DOM removal was most effective by MIEX-CI resin for GWTP-3, which had the lowest sulfate concentration. This is in agreement with previous literature highlighting MIEX® resin's affinity for sulfate. Additionally, aromatic carbon was preferentially removed compared to aliphatic carbon.

Single loading jar tests may underestimate resin removal efficiency. The multiple loading jar test procedure which is a better representation of full-scale ion exchange processes achieved higher removals compared to the single loading experiments. Thus, future research should follow the multiple loading method so as to not underestimate resin removal efficiency.

Combined ion exchange is an effective process for DOM and total hardness removal, and it can be performed within the same reactor. However, the 10× NaCl regenerant solution that is typically used is not effective for cation resin regeneration. A 100× NaCl solution is more effective for adequately cleaning the cation resin.

In general, the order of removal for combined ion exchange with a 10× NaCl regenerant solution was: $UV_{254} > DOC > \text{total hardness} > \text{sulfate} > \text{alkalinity}$. The order of removal for combined ion exchange with a 100× NaCl solution was: $\text{total hardness} > DOC > UV_{254} > \text{sulfate} > \text{alkalinity}$. Because Amberlite® 200C has a highly crosslinked structure, it is slightly more difficult to regenerate. Thus, a more concentrated regenerant solution is necessary.

For all groundwaters, $\geq 50\%$ of organic and/or inorganic fouling potential was removed by combined ion exchange. Thus, pretreatment using combined ion exchange could potentially reduce fouling of high-pressure membrane units. Additionally, $\geq 30\%$ of organic and inorganic fouling potential was reduced using a 100× NaCl solution. Thus, membrane fouling can be further reduced using a higher concentration regenerant solution. However, a cost-benefit analysis is necessary to determine if the production of a higher strength wastewater is worth the benefits of reduced membrane fouling.

Table 2-1. Resin physical and chemical characteristics.

Resin	Resin type	Functional groups	Total capacity (meq/mL)	Mobile counter ion
MIEX-Cl	Strong base	Quaternary amine	0.52	Cl ⁻
Amberlite® 200C	Strong acid	Sulfonic acid	1.70	Na ⁺
Purolite® C107E	Weak acid	Carboxylic acid	3.7	Na ⁺

Table 2-2. Raw groundwater characteristics.

Raw Water	pH	Total Hardness mg/L as CaCO ₃	Calcium Hardness mg/L as CaCO ₃	Alkalinity mg/L as CaCO ₃	Sulfate mg/L	UV ₂₅₄ cm ⁻¹	DOC mg C/L
GWTP-1 ^a	7.4	267	254	248	34.5	0.25	6.5
GWTP-2 ^b	7.1	437	415	317	134	0.08	3.0
GWTP-3 ^b	7.4	297	295	277	10.4	0.37	9.8

^a Values averaged from samples collected in September 2010 and January 2011

^b Values from sample collected in September 2010

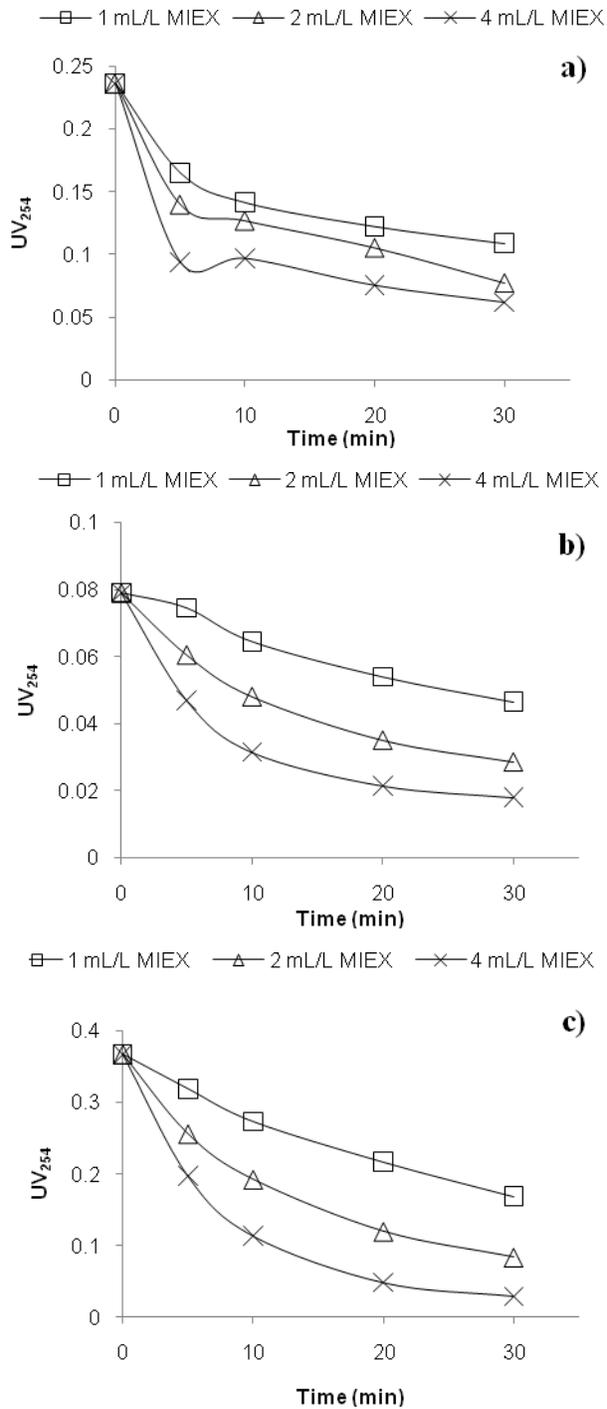


Figure 2-1. UV₂₅₄ removal for MIEX-Cl treatment of raw waters a) GWTP-1, b) GWTP-2, and c) GWTP-3.

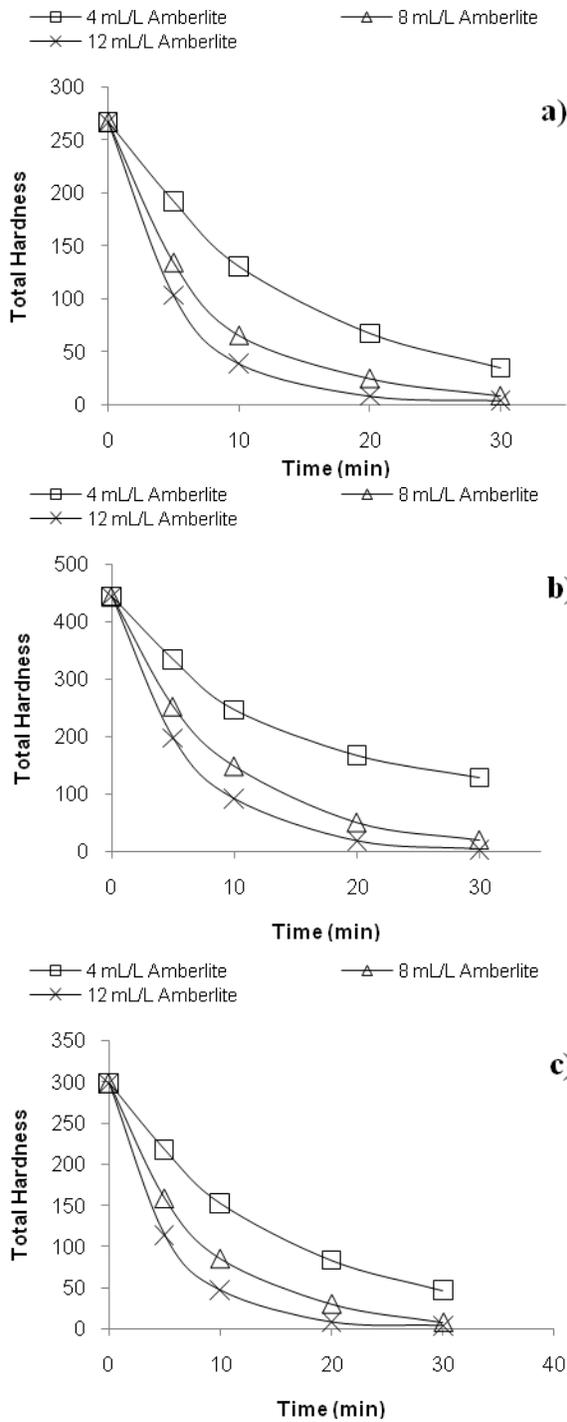


Figure 2-2. Total hardness removal for Amberlite® 200C treatment of raw waters a) GWTP-1, b) GWTP-2, c) GWTP-3.

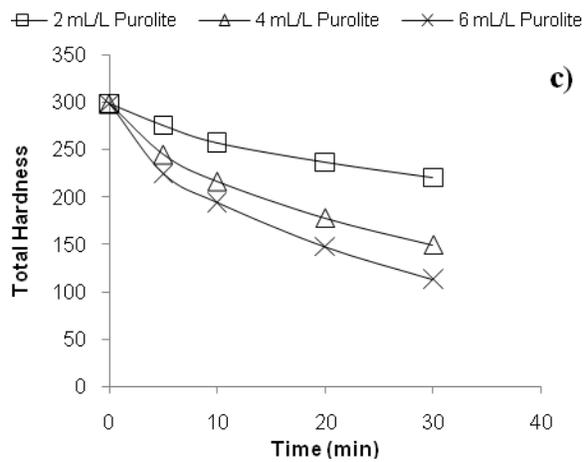
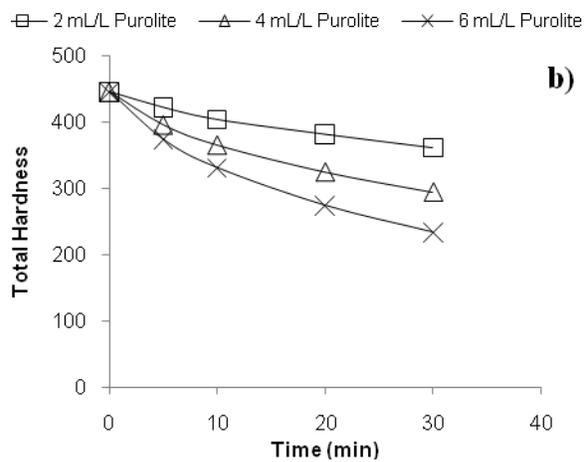
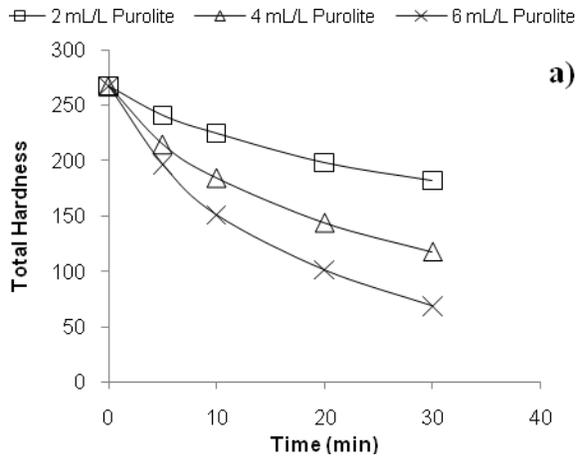


Figure 2-3. Total hardness removal for Purolite® C107E treatment of raw waters a) GWTP-1, b) GWTP-2, and c) GWTP-3.

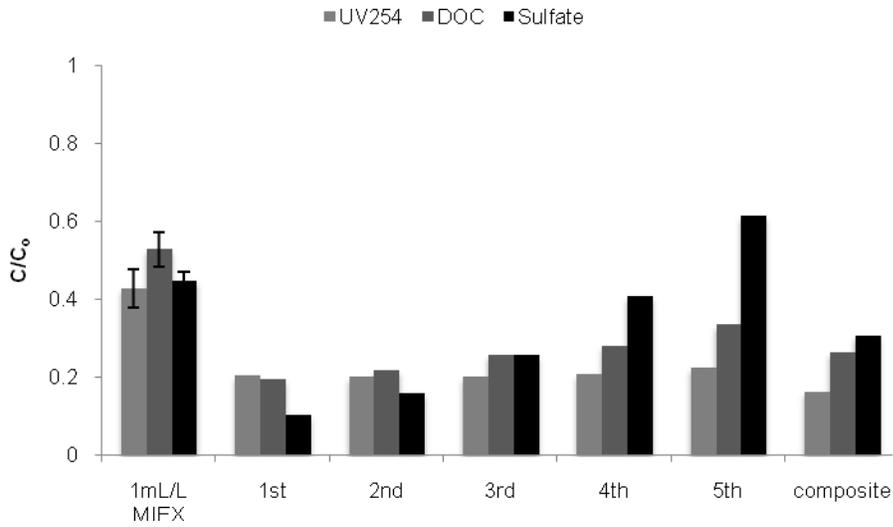


Figure 2-4. Comparison of results from 1 mL/L MIFX-CI GWTP-1 and anion exchange multiple loading with an effective resin dose of 1 mL/L MIFX-CI for GWTP-1, both with resin regenerated at 10× NaCl. The x-axis labels “1st”, “2nd”, etc. represent the location in the multiple loading sequence.

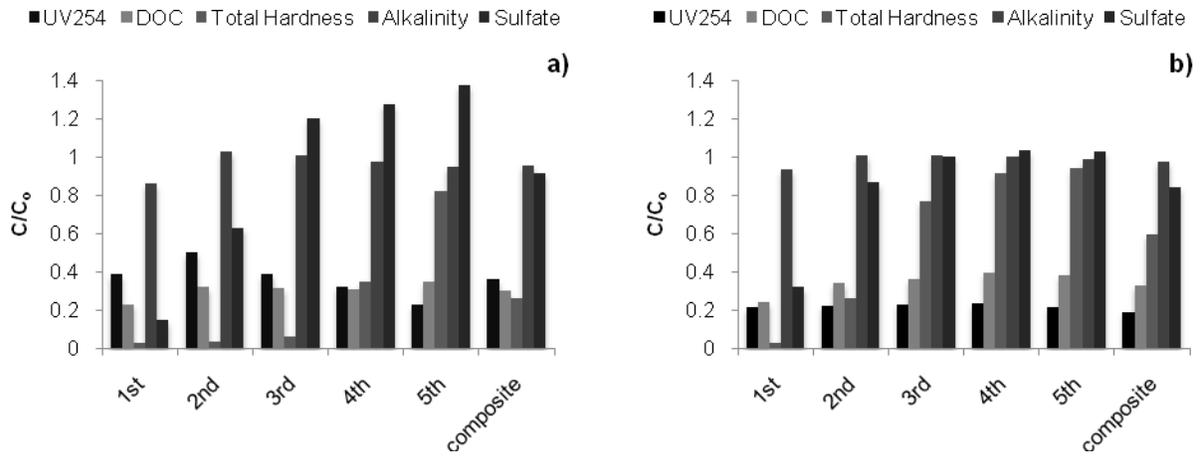


Figure 2-5. Combined ion exchange under multiple loading conditions for GWTP-1 water a) 1st loading cycle and b) 2nd loading cycle. Resin was regenerated at 10× NaCl for 20 mL/L Amberlite® 200C.

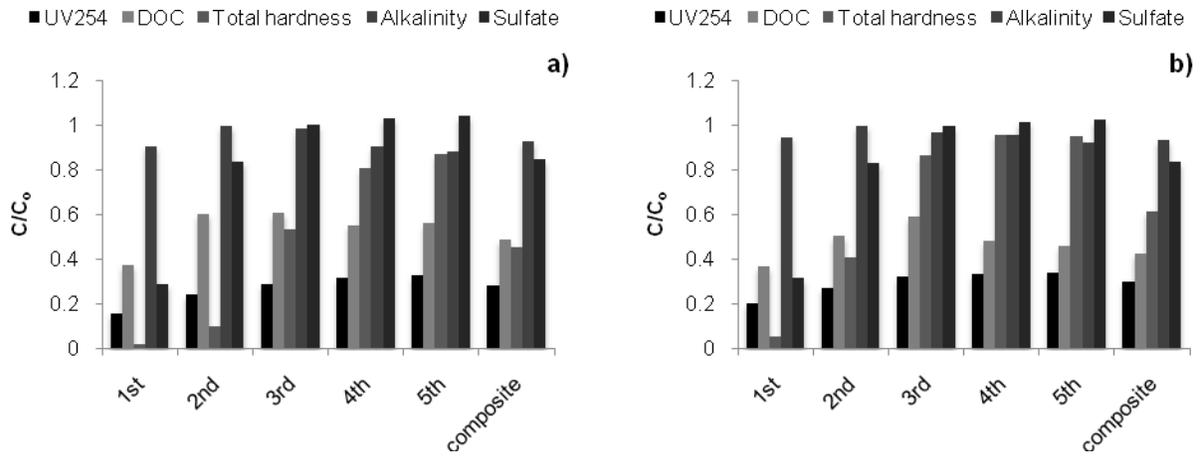


Figure 2-6. Combined ion exchange under multiple loading conditions for GWTP-2 water a) 1st loading cycle and b) 2nd loading cycle. Resin was regenerated at 10× NaCl for 20 mL/L Amberlite® 200C.

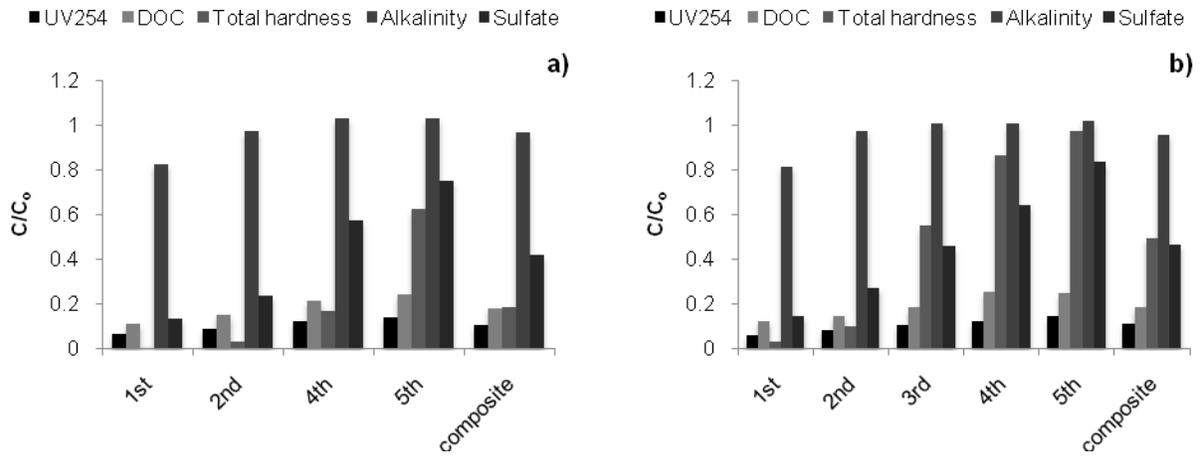


Figure 2-7. Combined ion exchange under multiple loading conditions for GWTP-3 water a) 1st loading cycle and b) 2nd loading cycle. Resin was regenerated at 10× NaCl for 20 mL/L Amberlite® 200C.

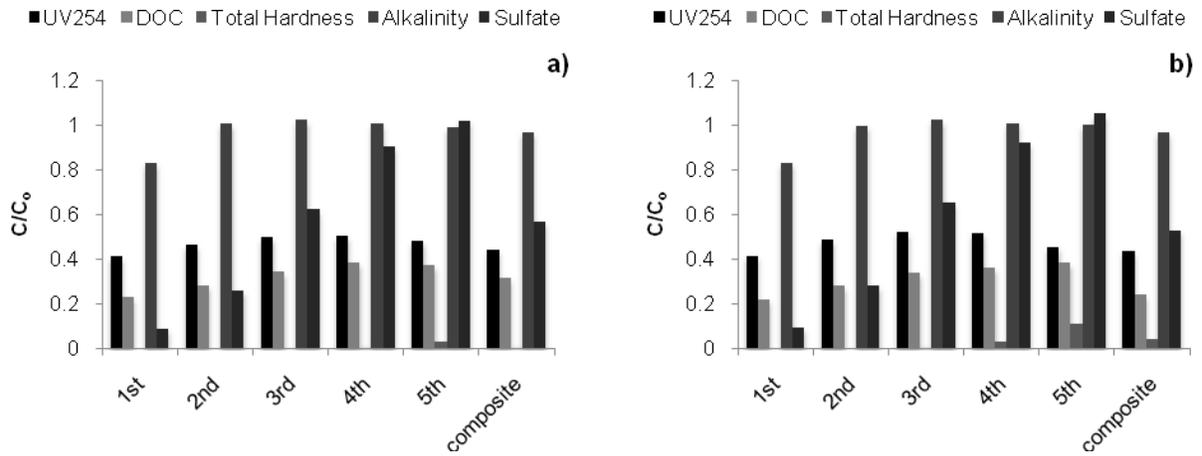


Figure 2-8. Combined ion exchange under multiple loading conditions for GWTP-1 water a) 1st loading cycle and b) 2nd loading cycle. Resin was regenerated at 100× NaCl for 20 mL/L Amberlite® 200C.

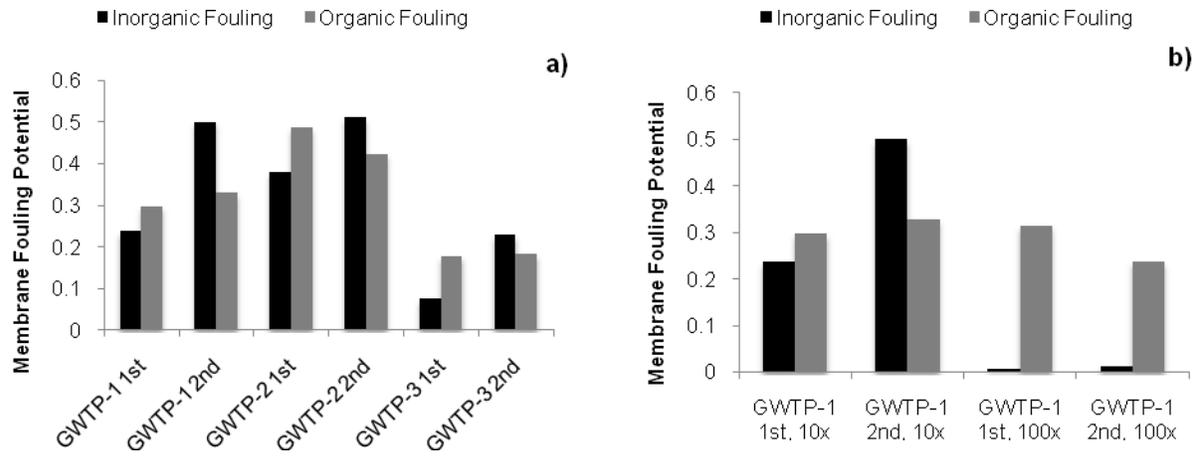


Figure 2-9. Effect of combined ion exchange treatment on theoretical membrane fouling. Values <1 indicate reduction in membrane fouling. Resin was regenerated at a) 10× NaCl for 20 mL/L Amberlite® 200C, and b) as designated on x-axis. “1st” and “2nd” designate the loading cycle that the data is from.

CHAPTER 3
EFFECT OF MEMBRANE CONCENTRATE CHEMISTRY ON COAGULATION,
SOFTENING, AND ANION EXCHANGE TREATABILITY

3.1. Membrane Concentrate Treatment Overview

Membrane processes are becoming a viable option for treatment of alternative water sources that are difficult to treat including brackish and reclaimed water. As coastal regions experience more saltwater intrusion from over-pumping groundwater, membrane treatment processes will become more prominent. Additionally, as water scarcity becomes more prevalent, the use of reclaimed water will increase and will eventually be used to augment potable water sources. Membrane treatment processes produce a purified permeate fraction and a concentrated waste stream. Despite the ease of implementing a membrane treatment system, one of the main obstacles is disposal of the membrane concentrate. There are numerous disposal methods including reuse, removal of contaminants, and discharge to groundwater or surface water bodies (Van der Bruggen et al., 2003). As membrane treatment plants move toward zero-liquid-discharge, treatment of membrane concentrate to remove contaminants and increase membrane recovery rates will become more important. Treating membrane concentrate before sending it through the next stage of membrane units can remove scaling components, thus improving flux rates (Heijman et al., 2009). Improving recovery rates typically results in decreased operating costs because the cost of disposing of membrane concentrate can be substantial in some cases (Ning and Troyer, 2009). Membrane concentrate treatment may also be necessary before final disposal to a wastewater treatment plant or deep-well injection so as to not harm the environment because chemicals used for pre-treatment of raw water and salinity become

concentrated in the waste stream and can be hazardous to receiving waters (Chelme-Ayala et al., 2009).

The composition of membrane concentrate depends on the source water characteristics, pre-treatment processes, membrane processes, and recovery rates (Chelme-Ayala et al., 2009; Squire, 2000). For example, source water that is high in dissolved organic carbon (DOC) and inorganic ions is typically considered as difficult to treat. It would be expected that source water that is difficult to treat would produce membrane concentrate that is even more difficult to treat due to the increased concentration of DOC and inorganic ions. Source water must be pretreated prior to membrane treatment in order to reduce membrane fouling and to achieve adequate recovery. Typical pre-treatment processes include particle removal by filtration and controlling precipitation on the membrane by addition of acid and antiscalant. The membrane pore size also has a considerable impact on the concentrate composition. Nanofiltration (NF) retains organic compounds with a molecular weight > 200–500 Da and multivalent ions (due to charge on membrane), whereas reverse osmosis (RO) retains small organic molecules and monovalent ions. Additionally, the recovery or flux rate of the membrane process will affect the concentration of feed water constituents in the concentrate (Squire, 2000).

Treatment of membrane concentrate can be divided into two categories: 1) removal of excess water (e.g., evaporation ponds) and 2) removal of specific components (Van der Bruggen et al., 2003). Focusing on removal of specific contaminants from membrane concentrate, various treatment methods can be implemented to remove components and improve flux rates, such as chemical

precipitation, ion exchange, oxidation, and adsorption (Chelme-Ayala et al., 2009). Precipitation by lime or base addition is the most common treatment method for membrane concentrate (Gabelich et al., 2007; Qu et al., 2009). Gabelich et al. (2007) considered intermediate treatment of concentrate from RO treatment of surface water by precipitation and showed that > 95% recovery was achieved by adding NaOH to primary RO concentrate, followed by secondary RO of the treated concentrate. This precipitation step removed scaling precursors including Ca^{2+} , Ba^{2+} , silica, and DOC. Several other studies have evaluated precipitation of NF and RO concentrate from treatment of waste streams including landfill leachate (Renou et al., 2008), wastewater treatment plant effluent (Mohammadesmaeili et al., 2010; Sperlich et al., 2010), and agricultural drainage (Rahardianto et al. 2010). There is limited data on ion exchange treatment of membrane concentrate, and to the best of our knowledge there are no previous studies evaluating magnetic ion exchange (MIEX®) treatment of membrane concentrate. Graf et al. (2010) investigated MIEX® treatment of landfill leachate and showed DOC removal of 20–30% was achieved even after 11 regeneration cycles. It was also found that MIEX® preferentially removed aromatic carbon from landfill leachate. Coagulation of landfill leachate, a concentrated waste stream, is common practice (Amokrane et al., 1997; Tatsi et al., 2003). However, there is limited data on coagulation of membrane concentrate. (Dialynas et al., 2008) investigated coagulation of concentrate from a membrane bioreactor fed by wastewater treatment plant effluent and achieved a maximum DOC removal of 52%. Finally, while there is limited data on coagulation and ion exchange of membrane concentrate, using these processes as pre-treatment for membrane processes is more widespread (Choi and Dempsey, 2004;

Cornelissen et al., 2010; Heijman et al., 2009). Choi and Dempsey (2004) used in-line coagulation to remove natural organic matter (NOM) from ultrafiltration (UF) feedwater. Heijman et al. (2009) and Cornelissen et al. (2010) evaluated ion exchange treatment prior to membrane filtration in order to improve recovery rates.

The drinking water industry is lacking a systematic study of membrane concentrate treatment, comparing individual established water treatment methods including coagulation, lime softening, and anion exchange. As previously noted, these treatment methods have been investigated for pre-treatment of membrane filtration. However, only softening has been investigated as an intermediate treatment step between primary and secondary membrane treatment. Intermediate treatment methods for membrane concentrate must be better investigated in order for membrane treatment processes to become more viable, particularly in inland areas. Thus, the goal of this work is to provide an improved understanding of membrane concentrate treatment with emphasis on the effect of dissolved organic matter (DOM), hardness, and SO_4^{2-} on coagulation, precipitation, and anion exchange processes. The specific objectives of this work are: (i) to compare chemistry of source waters and membrane concentrates, (ii) to evaluate coagulation, softening, and anion exchange as individual processes for treatment of membrane concentrate, (iii) to discuss the effect of the chemistry of membrane concentrate on treatability, (iv) to compare coagulation, softening, and anion exchange in terms of removal efficiency of DOM and inorganic ions, and (v) to discuss future work, such as membrane fouling potential and combined treatment processes.

3.2. Experimental

3.2.1. Sources of Membrane Concentrate

All membrane concentrate samples examined in this work were from municipal water treatment plants in Florida, USA. All membrane concentrate samples were collected using sampling ports on the membrane units, transported to the laboratory on ice, stored at 4°C, and tested within 3 months of collection. Membrane concentrate was collected from 5 different NF plants (NF-1, NF-2, NF-3, NF-4, NF-5) and 1 RO plant (RO-1). Membrane concentrate samples were collected twice from each facility during May and July 2010, except for NF-5 which was collected once during May 2010.

3.2.2. Treatment Chemicals

Ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$; Fisher Scientific; technical grade) was used for coagulation, calcium oxide (CaO; Acros Organics; 97+% purity) was used for lime softening, and MIEX[®] resin in the chloride form (MIEX-Cl; Orica Watercare) was used for anion exchange. Sodium carbonate (Na_2CO_3 ; Fisher Scientific; certified ACS) was used for alkalinity adjustment in select lime softening experiments. Standard chemicals used in analytical methods are described below. Deionized (DI) water was used to prepare all chemical reagents and standards, and to dilute samples when necessary. Glassware was cleaned with laboratory detergent, rinsed three times with DI water, and if necessary, soaked overnight in a 6% nitric acid solution.

3.2.3. Coagulation, Softening and Anion Exchange Jar Tests

A Phipps & Bird PB-700 jar tester was used to conduct various jar test treatments. The coagulation procedure was followed as described in Comstock et al. (2010). The doses investigated were 1.79, 4.48, and 8.95 mmol/L as Fe(III), which corresponds to 100, 250, and 500 mg/L as Fe(III), respectively. The lime softening procedure was

followed as described in Hsu and Singer (2009). The lime doses were 375, 625, and 1250 mg/L as CaO. These doses were achieved by adding 15 mL of a concentrated lime slurry of concentration 0.5, 0.74, and 1.49 M, respectively. For pre-softening alkalinity adjustment, sodium carbonate was added then mixed at 100 rpm until dissolved. The lime softening procedure was then followed as described above. The sodium carbonate doses were chosen based on the calcium hardness remaining in NF-1 and NF-4 concentrates treated by 625 mg/L CaO. Doses of 1.3 and 2.6 g/L sodium carbonate were used for NF-1 and NF-4, respectively. For the post-softening alkalinity adjustment experiments, the softening procedure was followed as described above. After settling, 900 mL of supernatant was decanted. Doses of 1.2 and 2.4 g/L sodium carbonate were added to NF-1 and NF-4 treated concentrate, respectively. The subsequent mixing was followed as described for the softening procedure. The anion exchange resin was measured as described in Apell and Boyer (2010). The doses were 5, 10, and 20 mL/L MIEX-Cl resin. Virgin resin was regenerated prior to use based on Apell and Boyer (2010) except the resin was mixed in the salt solution for 10 min at 100 rpm, and then rinsed in DI water for 10 min at 100 rpm using the jar tester described above. The anion exchange procedure was as follows: mix at 100 rpm for 30 min and settle for 5 min. Samples were collected at 5, 10, and 20 min (no settling) and 30 min (after settling). Samples at 5, 10, and 20 min were removed directly from the jar using a syringe fitted with a PVDF 0.45 μm filter (Millex-HV, Millipore) and analyzed for ultraviolet (UV) absorbance at 245 nm (UV_{254}) only.

3.2.4. Analytical Methods

All samples were analyzed for pH, DOC, UV₂₅₄, total hardness, calcium hardness, electrical conductivity, and color. TDS and fluorescence excitation-emission matrix (EEM) spectra were analyzed in all source waters and membrane concentrates. Softening samples were also analyzed for sulfate and alkalinity. Anion exchange samples were also analyzed for sulfate. Unfiltered water was used for pH measurements. All other measurements used samples filtered through 0.45 µm nylon membrane filters (Millipore). pH, DOC, UV₂₅₄, and color were analyzed as described in Comstock et al. (2010).

Total hardness was determined following Standard Methods 2340 (Clesceri et al., 1989). Due to the high hardness of membrane concentrate, dilutions were necessary for most samples. Reagents were made according to Standard Methods 2340. Calmagite was used as the indicator. Calcium hardness was determined following Standard Methods 3500-Ca D. However instead of using a 0.2% Eriochrome Blue Black R indicator, a 0.5% Eriochrome Blue Black R indicator was used to make the color change more noticeable. Dilutions were needed for most samples to prevent precipitation when increasing the pH. Alkalinity was determined by following Standard Methods 2320. Standard 0.02 N sulfuric acid was used as the titrant and bromcresol green was used as the indicator. For all titrations, once the end point was reached, this value was recorded and a few more drops of titrant were added to ensure that the color change was complete. SO₄²⁻ was measured by ion chromatography as described in Apell and Boyer (2010). An Orion model 115A+ TDS meter was used to measure total dissolved solids. The TDS meter was equipped with an Orion conductivity cell 011510. Fluorescence EEM spectra were collected on a Hitachi F-2500 fluorescence spectrophotometer using

a 1 cm quartz cell. Samples were diluted to $UV_{254} \approx 0.05$ to prevent inner filter effects (Mobed et al., 1996) and scanned at 5 nm increments over an excitation (EX) wavelength = 220–400 nm and at 2 nm increments over an emission (EM) wavelength = 250–550 nm. The raw EEMs were processed in MATLAB (The Math-Works) as described elsewhere (Comstock et al., 2010).

3.3. Results

3.3.1. Chemistry of Source Waters and Membrane Concentrates

Water quality and concentration factors (CFs) for the membrane concentrates are given in Table 3-1. TDS was used as a surrogate for inorganic ions; sulfate was used as a surrogate for divalent inorganic anions; hardness was used as a surrogate for divalent inorganic cations; and color, UV_{254} , and DOC were used as surrogates for DOM. The CF for each water quality parameter was calculated by dividing the concentration in membrane concentrate by the concentration in source water. A theoretical CF can be calculated based on the percent recovery of the membrane process with the assumption of complete rejection by the membrane. The theoretical CFs for 80, 85, and 90% recovery are 5, 6.7, and 10. The water quality data and CFs are discussed in the context of each water treatment plant in the subsequent paragraphs.

NF-1 uses source water from the Biscayne Aquifer. Water is withdrawn from wells approximately 3–60 m below ground and 12 million gallons per day (MGD) (45 megaliters per day (MLD)) is produced by NF. Source water that passes through the NF treatment train is pretreated by acid addition (93% concentrated sulfuric acid; target pH of 5.8) and filtration (sand separators and 5 μ m cartridge filters). The typical recovery rate is 80%, and currently the membrane concentrate is disposed of by deep-well

injection. The CFs for all parameters were very similar with a range of 3.8–5.0, as shown in Table 3-1. The trend for CFs for NF-1 was: DOM \approx hardness > sulfate > alkalinity > TDS. The DOM parameters were similarly concentrated from the source water, which indicates that this membrane process does not preferentially reject aromatic carbon. The CFs for hardness and DOM approached the theoretical CF of 5.0 for NF-1 membrane concentrate.

NF-2 uses source water from the Biscayne Aquifer. Water is withdrawn from wells approximately 18–45 m below ground and 14 MGD (53 MLD) is produced by NF. Source water that passes through the NF treatment train is pretreated by acid addition (93% concentrated sulfuric acid; target pH of 6.6), antiscalant addition (Nalco PC-1850T; applied dose of 1.5 mg/L), and filtration (5 μ m cartridge filters). The typical recovery rate is 90%, and currently the membrane concentrate is discharged to a wastewater treatment plant. NF-2 source water had a range of CFs of 5.1–10.0, as shown in Table 3-1. The trend for CFs for NF-2 was: sulfate > DOM \approx hardness > alkalinity > TDS. The DOM parameters had CFs of 6.0–7.1. DOC had a higher CF (7.1) than UV₂₅₄ (6.4) and color (6.0) indicating aliphatic carbon was rejected more than aromatic carbon. The CF for sulfate approached the theoretical CF of 10.0 for NF-2.

NF-3 uses source water from the Biscayne Aquifer; 40 MGD (151 MLD) is produced by NF. Source water that passes through the NF treatment train is pretreated by filtration (pressure filters and 5 μ m cartridge filters). The typical recovery rate is 80–85%, and currently the membrane concentrate is discharged to a wastewater treatment plant located in the same complex. NF-3 source water had a range of CFs of 3.3–5.6, as shown in Table 3-1. The trend for CFs for NF-3 was: DOM > sulfate > hardness \approx

alkalinity > TDS. There was no clear trend for rejection of aromatic versus aliphatic carbon based on the CFs for DOM parameters. The CFs for divalent anion and DOM approached the theoretical CF of 5.0–6.7 for NF-3 membrane concentrate.

NF-4 uses source water from the lower Tamiami Aquifer; 12 MGD (45 MLD) is produced by NF. Source water that passes through the NF treatment train is pretreated by acid addition (93% concentrated sulfuric acid; target pH of 5.2), antiscalant addition (American Water Chemicals A102plus; applied dose of 1.7 mg/L), and filtration (5 μ m cartridge filters). The typical recovery rate is 85%, and currently the membrane concentrate is disposed of by deep-well injection. NF-4 source water had a wide range of CFs of 0.2–77.0, as shown in Table 3-1. The trend for CFs for NF-4 was: sulfate > hardness > DOM > TDS > alkalinity. Sulfate had a CF of 77.0, which was 10x greater than the theoretical CF of 6.7 for NF-4. The antiscalant used at NF-4 may be a possible source of SO_4^{2-} because it has sulfonate functional groups. DOC and UV_{254} had similar CFs indicating that aromatic carbon was not preferentially rejected. The CFs for divalent cations and DOM exceeded the theoretical CF of 6.7 for NF-4.

NF-5 uses source water from the lower Tamiami Aquifer. Water is withdrawn from wells 18m below ground and 0.99 MGD (3.7 MLD) is produced by NF. Source water that passes through the NF treatment train is pretreated by acid addition (93% concentrated sulfuric acid), antiscalant addition (American Water Chemicals A102plus; applied dose of 2.5 mg/L), and filtration (5 μ m cartridge filters). The typical recovery rate is 85%, and currently the membrane concentrate is disposed of by deep-well injection. NF-5 source water had a range of CFs of 3.7–21, as shown in Table 3-1. The trend for CFs for NF-5 was: sulfate > DOM > hardness > TDS > alkalinity. The CF for sulfate was

21, which is greater than the theoretical CF of 6.7 for NF-5. Both NF-4 and NF-5 use the same antiscalant, which may be a possible source of sulfate. There was no clear trend for rejection of aromatic versus aliphatic carbon based on CFs for DOM parameters. The CFs for DOM parameters approached the theoretical CF of 6.7 for NF-5.

RO-1 uses source water from the upper Floridan Aquifer; 6 MGD (23 MLD) is produced by RO. Source water that passes through the RO treatment train is pretreated by acid addition (sulfuric acid; target pH of 5.0), antiscalant addition (GE Betz Hypersperse MDC 700; applied dose of 2.0 mg/L), and filtration (manganese greensand pressure filters and 5 µm cartridge filters). The typical recovery rate is 80%, and currently the membrane concentrate is treated and disposed of through a reclaimed water system for irrigation. RO-1 source water had a range of CFs of 1.2–5.6, as shown in Table 3-1. The trend for CFs for RO-1 was: hardness > DOM (excluding color) > alkalinity ≈ sulfate > TDS > color. UV₂₅₄ and DOC had very similar CFs indicating that aromatic carbon is not preferentially rejected. The CFs for hardness approached the theoretical CF of 5.0 for RO-1.

Fluorescence EEM spectra for all source waters and untreated membrane concentrates are shown in Figure 3-1. Source and concentrate EEMs for samples from all water treatment plants had peaks at comparable EX/EM wavelengths, indicating that DOM characteristics of each source and corresponding concentrate were constant.

3.3.2. Coagulation of Membrane Concentrate

The results of coagulation jar tests using ferric sulfate and membrane concentrates are shown in Figure 3-2. NF-2, NF-3, NF-5, and RO-1 all showed increasing DOC removal as the ferric sulfate dose was increased. In contrast, NF-1 and

NF-2 showed maximum DOC removal at the lowest ferric sulfate dose. The difference in coagulation performance between the concentrates was examined by tracking the pH after coagulation, as shown in Figure 3-3. Again, NF-1 and NF-4 had a different trend when compared to the other concentrates. The pH for these concentrates was much lower for all coagulant doses because of the low buffering capacity of the membrane concentrates. The alkalinity values of NF-1 and NF-4 were 270 and 62 mg/L as CaCO₃, respectively, whereas the other concentrates had alkalinity values ranging from 925–1170 mg/L as CaCO₃. As expected, total hardness removal was negligible ranging from a 2% decrease to a 1% increase (results not shown). Sulfate was not measured for samples treated by coagulation because using ferric sulfate as the coagulant increased the sulfate concentration. In general, the order of removal for coagulation treatment was as follows: color > UV₂₅₄ > DOC, and total hardness was not affected. Greater removal of aromatic vs. aliphatic carbon, represented by color and UV₂₅₄ data, is consistent with coagulation of natural waters (Archer and Singer, 2006). However, this trend is not applicable to NF-1, NF-4, and RO-1. The low alkalinity of NF-1 and NF-4 caused a decrease in pH at high coagulant doses, resulting in dissolution of Fe(III) which caused an increase in UV₂₅₄ (Weishaar et al., 2003). RO-1 had the next lowest alkalinity after NF-1 and NF-4, and thus the pH of RO-1 was not affected until the highest dose of ferric sulfate was applied, resulting in normalized UV₂₅₄ and color values greater than 1.

3.3.3. Softening of Membrane Concentrate

The results of the softening jar tests using lime and membrane concentrates are shown in Figure 3-4. NF-2, NF-3, NF-5 and RO-1 showed optimum removal of total hardness at a dose of 625 mg/L CaO. NF-1 and NF-4 had increasingly poor removal as the CaO dose was increased, indicating that the added Ca²⁺ did not precipitate. Poor

hardness removal for NF-1 and NF-4 is likely attributed to their low alkalinity values because there was not sufficient carbonate source for CaCO_3 to precipitate. Thus, better hardness removal could be achieved by alkalinity adjustment in conjunction with lime softening. All concentrates showed increasing DOC removal with increasing CaO dose. DOC removal was greater than total hardness removal at the highest CaO dose for membrane concentrate in Figure 3-4, parts A-D, whereas DOC removal was greater than total hardness removal at all CaO doses for membrane concentrate in Figure 3-4, parts E-F. NF-3 had the highest DOC removal of 70% for a CaO dose of 1250 mg/L. Maximum DOC removal at the highest lime dose is likely due to excess Ca^{2+} forming complexes with DOM (Russell et al., 2009). Similar removal trends were also seen for UV_{254} and color for the three doses (results not shown). Sulfate removal was consistent for all three lime doses (results not shown) and ranged from 0–15%. In general, the order of removal was as follows: total hardness ~ calcium hardness > color > UV_{254} > DOC > sulfate. However, this trend was not applicable to NF-1 and NF-4 because of their low alkalinity values as previously stated. Greater removal of aromatic vs. aliphatic carbon by lime softening of membrane concentrate was consistent with softening of natural waters (Thompson et al., 1997).

To further investigate hardness removal, alkalinity adjusted softening experiments were performed for NF-1 and NF-4. The results of softening jar tests using lime and membrane concentrates with alkalinity adjustment are shown in Figure 3-5. Both pre- and post- softening alkalinity adjustment resulted in 99% total hardness removal for NF-1 and NF-4 compared to softening with unadjusted alkalinity, which increased total hardness. Pre-softening alkalinity adjustment slightly decreased DOC

removal as compared to softening with unadjusted alkalinity because addition of soda ash increased total carbonate, which caused a decrease in free Ca^{2+} able to form complexes with DOM (Lin et al., 2005; Russell et al., 2009). Post-softening alkalinity adjustment achieved 55% and 30% DOC removal for NF-1 and NF-4, respectively, compared to 50% and 28% DOC removal for softening without alkalinity adjustment for NF-1 and NF-4, respectively.

3.3.4. Anion Exchange of Membrane Concentrate

Kinetic data for UV_{254} absorbance for anion exchange of all membrane concentrates is shown in Figures 3-6. All MIEX-Cl doses followed a similar trend. However, 20 mL/L MIEX-Cl achieved higher removal at a quicker rate. Near maximum removal of UV_{254} was achieved in a contact time of 5 min for all concentrates. NF-1 and NF-4 had lower UV_{254} removal and a slower rate of removal compared to the other concentrates. The removal trends seen for all membrane concentrates were similar to that of raw drinking water described in Boyer and Singer (2005). Thus, ideas and practices from MIEX® treatment of raw drinking water are applicable to treating concentrated waste streams, such as membrane concentrate.

Figure 3-7 shows DOC removal for MIEX-Cl treatment of membrane concentrate. For all membrane concentrates, increasing MIEX-Cl dose resulted in increasing DOC removal. Overall, NF-3 had the optimum DOC removal of 75% at a dose of 5 mL/L MIEX-Cl. Although NF-3 did achieve 87% DOC removal at 20 mL/L MIEX-Cl, a 12% increase in DOC removal does not justify the need for 4× the resin dose. Additionally, 5 mL/L MIEX-Cl is a realistic design dose. NF-4 had the lowest DOC removal for all three doses. Because MIEX-Cl is an anion exchange resin, other anions present in the water

at high concentrations can compete with DOC for resin exchange sites (Boyer and Singer, 2006). Figure 3-8, parts A-B shows DOC removal as a function of sulfate concentration and TDS, respectively. In general as sulfate concentration increased, DOC removal decreased in Figure 3-8, part A. The minimum DOC removal of 33% correlated to the highest sulfate concentration of 2600 mg/L. However this relationship was more defined for DOC removal as a function of TDS as shown in Figure 3-8, part B. As TDS increased, DOC removal decreased. NF-4 deviated from this trend because it had the second highest TDS but the lowest DOC removal. This is likely attributed to the very high sulfate content and MIEX® resin's preference for sulfate over other anions (Boyer and Singer, 2006). The TDS values covered a wider range than sulfate concentration, which better correlated to the spread of DOC removals. TDS had a stronger association with DOC removal compared to sulfate because TDS includes sulfate and all other anions present in membrane concentrate. Figure 3-8, parts A-B show that sulfate and other anions were being removed from the membrane concentrate, and thus was competing with DOC for resin exchange sites. In general, the order of removal was as follows: color > UV_{254} > DOC > sulfate, and total hardness was not affected.

3.4. Discussion

3.4.1. Effect of Membrane Concentrate Chemistry

DOM, hardness, alkalinity, sulfate, and TDS are all important parameters to consider during treatment of drinking water and membrane concentrate. Specific ultraviolet absorbance at 254 nm ($SUVA_{254} = UV_{254}/DOC$) is a useful parameter for evaluating the chemistry and treatability of DOM. $SUVA_{254}$ values for membrane concentrate ranged from 2.2–3.6. Based on $SUVA_{254}$, RO-1 and NF-4 membrane

concentrate DOM was more microbially influenced ($SUVA_{254} < 3 \text{ L/mg/m}$), and all other membrane concentrate DOM was intermediate, both microbially and terrestrially influenced ($3 < SUVA_{254} < 4 \text{ L/mg/m}$) (Boyer et al., 2008). In general, all membrane concentrates had intermediate SUVA values, which indicated a mix of microbially and terrestrially derived DOM. Fluorescence excitation-emission-matrix (EEM) spectra were analyzed for all source water and membrane concentrate to provide additional insight into the chemistry of membrane concentrate DOM. All membrane concentrate EEMs had one fluorescence peak known as peak A, EX/EM = 217–261/395–460 (Hudson et al., 2008). Peak A is associated with terrestrial, humic-like DOM that is common in natural surface waters. The fluorescence data suggested that all membrane concentrate DOM was more terrestrially influenced than microbially influenced. Thus, $SUVA_{254}$ indicated intermediate DOM whereas fluorescence EEM spectra indicated more terrestrial DOM. Similarities and differences in DOM chemistry did not have a notable effect on membrane concentrate treatment. Hardness did not affect treatment of membrane concentrate. Alkalinity had a major impact on both coagulation and softening because of pH changes and insufficient carbonate concentration for precipitation, respectively. Sulfate concentration and TDS had an impact on DOC removal by anion exchange due to competition for resin exchange sites.

Another possible factor in concentrate treatment efficiency is the use of antiscalants prior to membrane treatment. (Greenlee et al., 2010) showed that antiscalants could interfere with precipitation during softening of membrane concentrate. However, water chemistry and properties of the concentrate may have had a bigger impact on treatment efficiency. For example, NF-4 and NF-5 both used AWC A102plus

as their antiscalant, yet they reacted very differently to coagulation and softening treatment due to the source water chemistry (i.e., NF-4 has low alkalinity). Additionally NF-1 and NF-3 did not use antiscalants, yet they reacted very differently to coagulation and softening treatment because NF-1 has low alkalinity. NF-3 also achieved better DOC removal by MIEX® treatment compared to NF-1, which was likely attributed to NF-1 having a high concentration of sulfate. In general, the results of this work show that source water characteristics had a greater effect on treatment efficiency compared to pre-treatment chemical and processes, such as antiscalants.

3.4.2. Comparison of Coagulation, Softening and Anion Exchange

The order of removal of DOM parameters including color, UV_{254} and DOC was: anion exchange > coagulation > softening. Anion exchange had a maximum color removal of 98%; coagulation had a maximum color removal of 95%; and softening had a maximum color removal of 83%. Anion exchange also had a maximum UV_{254} removal of 95%; coagulation had a maximum UV_{254} removal of 90%; and softening had a maximum UV_{254} removal of 80%. Anion exchange had a maximum DOC removal of 87%; coagulation had a maximum DOC removal of 84%; and softening had a maximum DOC removal of 66%. NF-2 had the maximum removal of all DOM parameters for coagulation; NF-3 had the maximum removal of all DOM parameters for softening; and NF-5 had the maximum removal of color, whereas NF-3 had the maximum removal of UV_{254} and DOC for anion exchange. Thus, if aromatic carbon and maximum DOC removal are being targeted, anion exchange is the best treatment method when compared to coagulation and softening.

Softening achieved the highest removal of total hardness. Coagulation and anion exchange did not affect total hardness removal. Maximum total hardness removal was achieved for NF-3 at 625 mg/L CaO and the corresponding DOC removal was 24%. Of the three treatment process evaluated, softening was the only process that removed both organic and inorganic constituents. Therefore, if both total hardness and DOM removal is a priority, softening is the best treatment method compared to coagulation and anion exchange. Softening was the most sensitive process to membrane concentrate chemistry compared to coagulation and anion exchange. The total hardness of NF-1 and NF-4 was actually increased for 625 and 1250 mg/L CaO because of their low alkalinity values.

Sulfate is another important component of membrane concentrate because of its ability to form precipitates with divalent cations, such as calcium sulfate and barium sulfate (Jarusutthirak et al., 2007; Shih et al., 2005). Thus, sulfate removal before secondary membrane treatment could improve flux rates. The order of removal for sulfate was: anion exchange > softening, and coagulation increased the sulfate concentration. Sulfate removal by MIEX-Cl treatment varied from 0–81%, depending on concentrate chemistry and resin dose. Softening achieved more consistent sulfate removal varying from 0–15%, and sulfate removal was independent of CaO dose.

3.4.3. Theoretical Membrane Fouling Potential

The overall goal of treating membrane concentrate is to be able to send treated concentrate through a secondary membrane process to decrease the amount of liquid waste generated at a water treatment facility. The membrane fouling potential of treated concentrate is an important parameter to evaluate when determining the best intermediate treatment process for membrane concentrate. Figure 3-9 shows the

theoretical membrane fouling potential associated with concentrate treated by coagulation, softening and anion exchange as based on work by Apell and Boyer (2010). The membrane fouling potentials were defined as: inorganic fouling potential = $([Ca^{2+}][SO_4^{2-}])/([Ca^{2+}]_0[SO_4^{2-}]_0)$ and organic fouling potential = $[DOC]/[DOC]_0$, where the subscript 0 indicates initial concentration. The fouling potentials were calculated for NF-5 at the middle doses of each treatment process. As shown in Figure 3-9, anion exchange results in the lowest overall membrane fouling potential with lower organic fouling potential than inorganic fouling potential. Coagulation is not a good choice for treating membrane concentrate because it does not remove hardness and it adds sulfate, which compounds to produce a large inorganic membrane fouling potential. Softening has an overall membrane fouling potential close to that of anion exchange, but the organic fouling potential after softening treatment is higher than that of anion exchange. Because anion exchange and softening target different components of the membrane fouling potential, it can be inferred that combined treatment processes that will target both inorganic and organic foulants, resulting in the least membrane fouling and the highest flux rates. Thus, in order to have an effective intermediate treatment process, combining treatment processes that remove different membrane fouling constituents is necessary.

3.5. Membrane Concentrate Treatment Summary

This work provides a systematic study of common drinking water treatment processes for the treatment of NF and RO membrane concentrates. The treatment processes investigated were coagulation with ferric sulfate, softening with CaO, and anion exchange using MIEX® resin. The major findings are as follows:

Traditional water treatment methods can be used to effectively remove organic and/or inorganic fouling components from concentrated waste streams. The chosen treatment processes strongly depends on the chemistry of the concentrate.

For anion exchange treatment, the order of removal was color > UV₂₅₄ > DOC > sulfate. This trend is also seen in drinking water treatment. Anion exchange removed organic, and to a lesser extent inorganic foulants. Anion exchange was more robust compared to coagulation and softening, in terms of variation in concentrate chemistry, such as alkalinity.

For lime softening, the order of removal was: total hardness > color > UV₂₅₄ > DOC > sulfate. Concentrate with insufficient alkalinity to form CaCO₃ (s) required soda ash (sodium carbonate) to achieve sufficient hardness removal. DOM removal was the same with and without alkalinity adjustment.

For coagulation, the order of removal of DOM parameters was: color > UV₂₅₄ > DOC. This trend was not applicable to concentrates with low alkalinity at high ferric sulfate doses due to dissolution of Fe(III). Coagulation is not a promising process for treatment of membrane concentrate because the method is sensitive to alkalinity and pH, and does not remove inorganic foulants.

DOM properties and hardness did not affect treatment of membrane concentrate. Characteristics including alkalinity, sulfate concentration, and TDS did impact the effectiveness of treatment processes, with coagulation and softening affected by alkalinity and anion exchange affected by sulfate and TDS.

The order of removal of DOM parameters was: anion exchange > coagulation > softening. Total hardness was removed by softening only. Anion exchange and

softening removed sulfate. Anion exchange achieved greater removals of sulfate, whereas softening was independent of dose and concentrate chemistry.

Combined treatment processes that target both organic and inorganic foulants would result in the highest recovery rates. Anion exchange followed by softening and combined anion/cation exchange are two combined treatment processes that should be evaluated for membrane concentrate treatment.

Table 3-1. Water quality and source water concentration factors for membrane concentrates used in physical-chemical treatment studies^a.

Raw Water	pH	TDS mg/L	Alkalinity mg/L as CaCO ₃	Sulfate mg/L	Total Hardness mg/L as CaCO ₃	Calcium Hardness mg/L as CaCO ₃	Color Pt-Co
NF-1	6.3	979 (3.8)	270 (4.0)	639 (4.2)	1071 (5.0)	1009 (4.7)	368 (4.7)
NF-2	6.8	1380 (5.1)	1170 (5.4)	278 (10)	1596 (6.6)	1373 (6.1)	409 (6.0)
NF-3	7	940 (3.3)	950 (4.2)	73 (5.0)	1050 (4.2)	978 (4.0)	454 (5.6)
NF-4	7.2	1880 (4.6)	62 (0.2)	2646 (77)	2505 (7.3)	1914 (6.9)	243 (6.5)
NF-5	7.1	1180 (3.9)	1050 (3.7)	160 (21)	1454 (5.1)	1202 (5.0)	546 (6.4)
RO-1	6.8	2190 (4.1)	925 (4.8)	165 (4.7)	1717 (5.6)	1404 (5.1)	46 (1.2)

^a Value in membrane concentrate (concentration factor = membrane concentrate/source water).

Table 3-1. Continued

Raw Water	UV ₂₅₄ cm ⁻¹	DOC mg C/L
NF-1	1.65 (4.7)	45.5 (4.8)
NF-2	1.90 (6.4)	54.0 (7.1)
NF-3	2.32 (5.0)	67.0 (5.4)
NF-4	1.85 (7.3)	62.4 (7.4)
NF-5	2.70 (6.0)	78.5 (6.4)
RO-1	0.28 (5.2)	13.0 (5.1)

^a Value in membrane concentrate (concentration factor = membrane concentrate/source water).

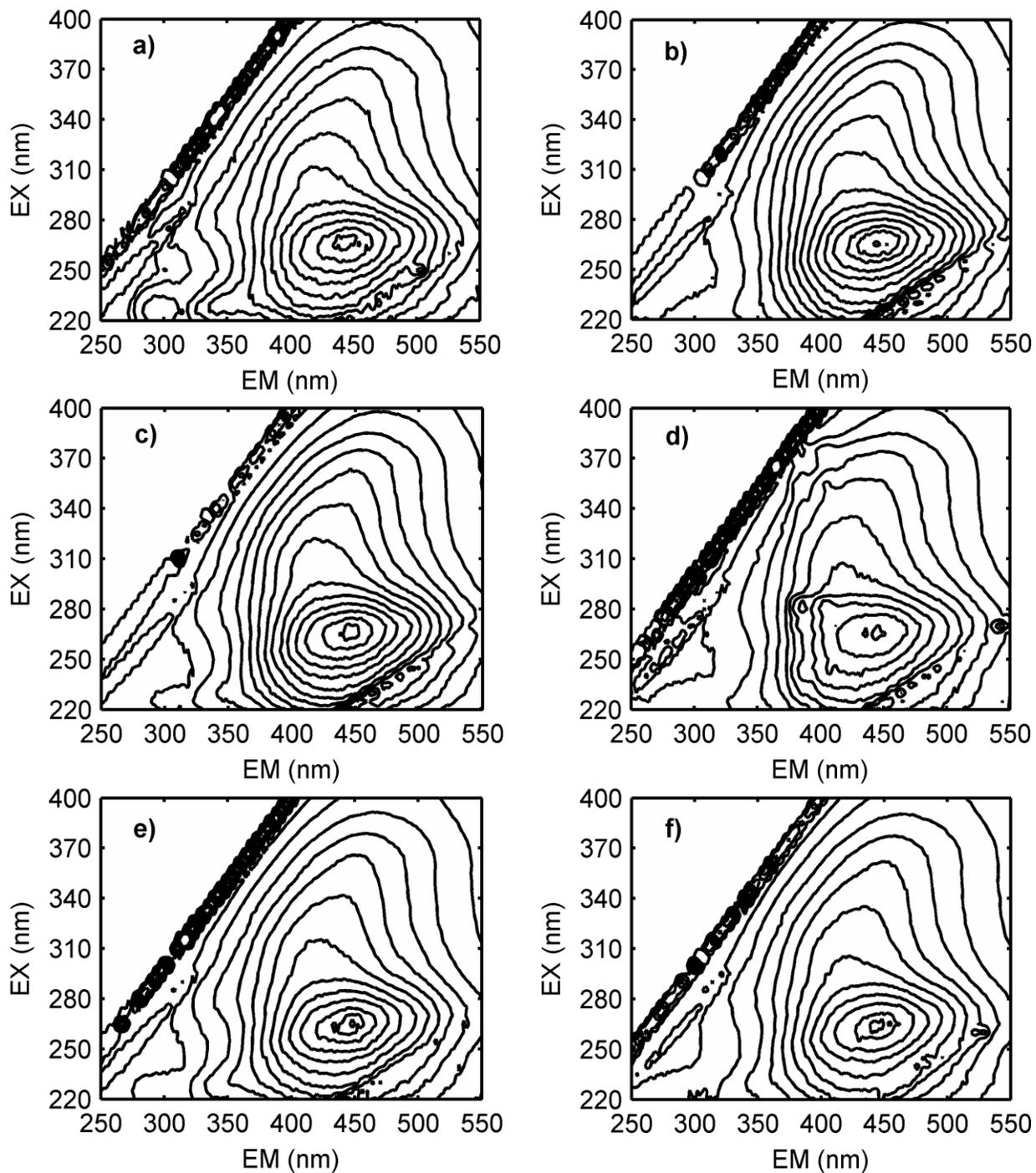


Figure 3-1. Fluorescence EEM spectra for NF-1 (a) source water and (b) membrane concentrate; NF-2 (c) source water and (d) concentrate; NF-3 (e) source water and (f) concentrate; NF-4 (g) source water and (h) concentrate; NF-5 (i) source water and (j) concentrate; and RO-1 (k) source water and (l) concentrate.

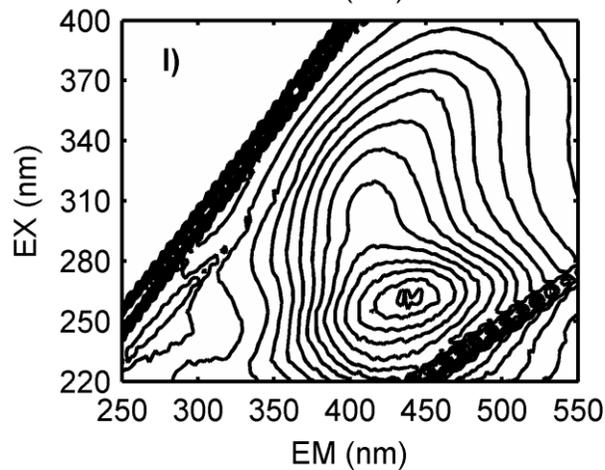
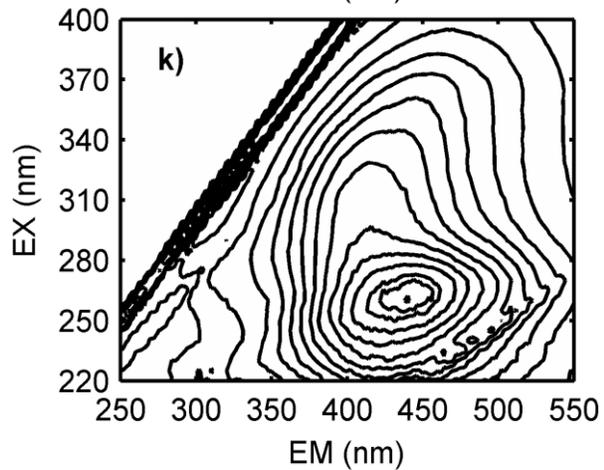
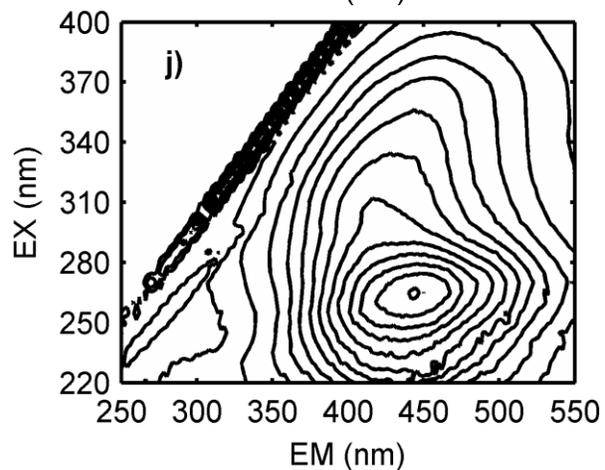
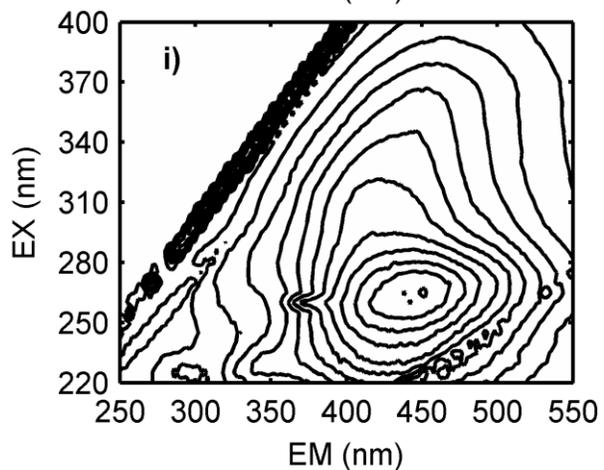
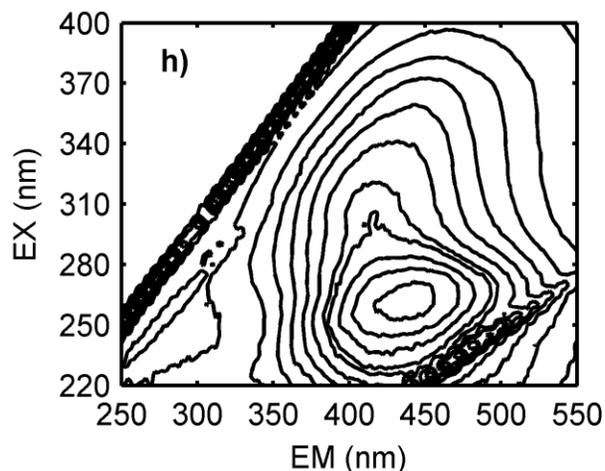
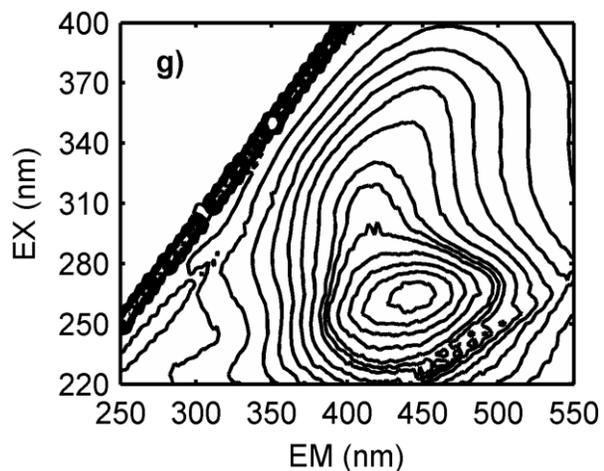


Figure 3-1. Continued

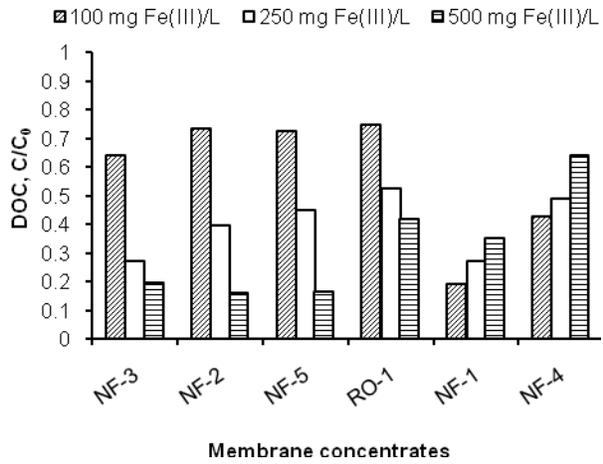


Figure 3-2. Final normalized concentrations of DOC following ferric sulfate coagulation of membrane concentrate.

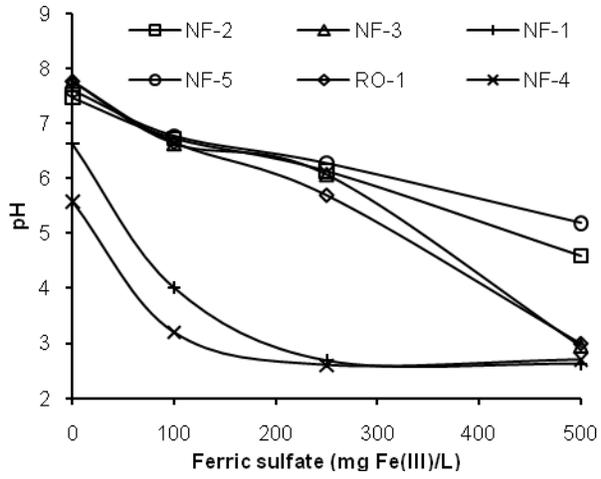


Figure 3-3. Final pH following ferric sulfate coagulation of membrane concentrate.

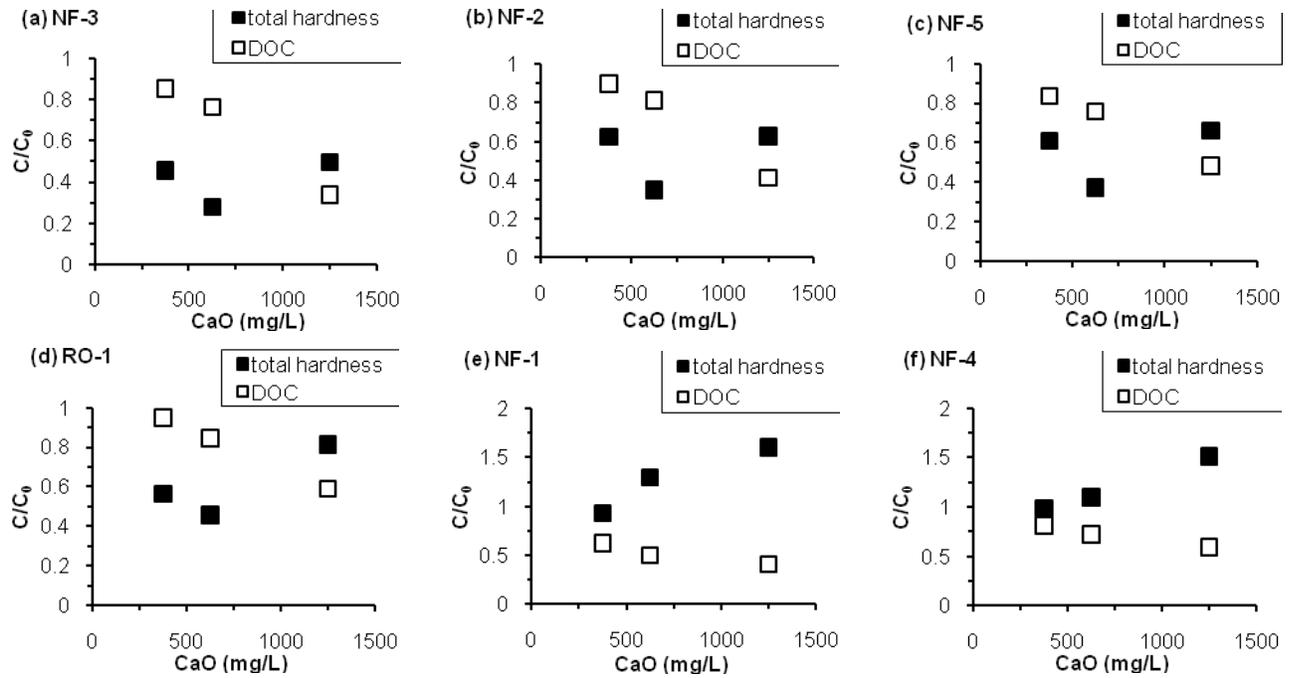


Figure 3-4. Effectiveness of lime softening for removal of total hardness and DOC from membrane concentrate.

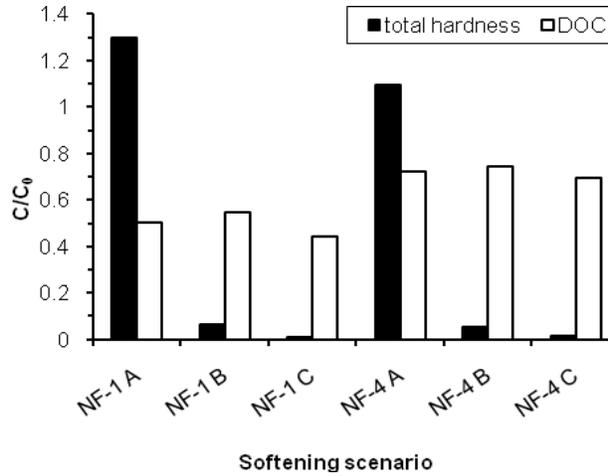


Figure 3-5. Effect of alkalinity adjustment on lime softening performance. All samples followed the same softening procedure (625 mg/L as CaO). A: no alkalinity adjustment; B: pre-softening alkalinity adjustment; C: post-softening alkalinity adjustment.

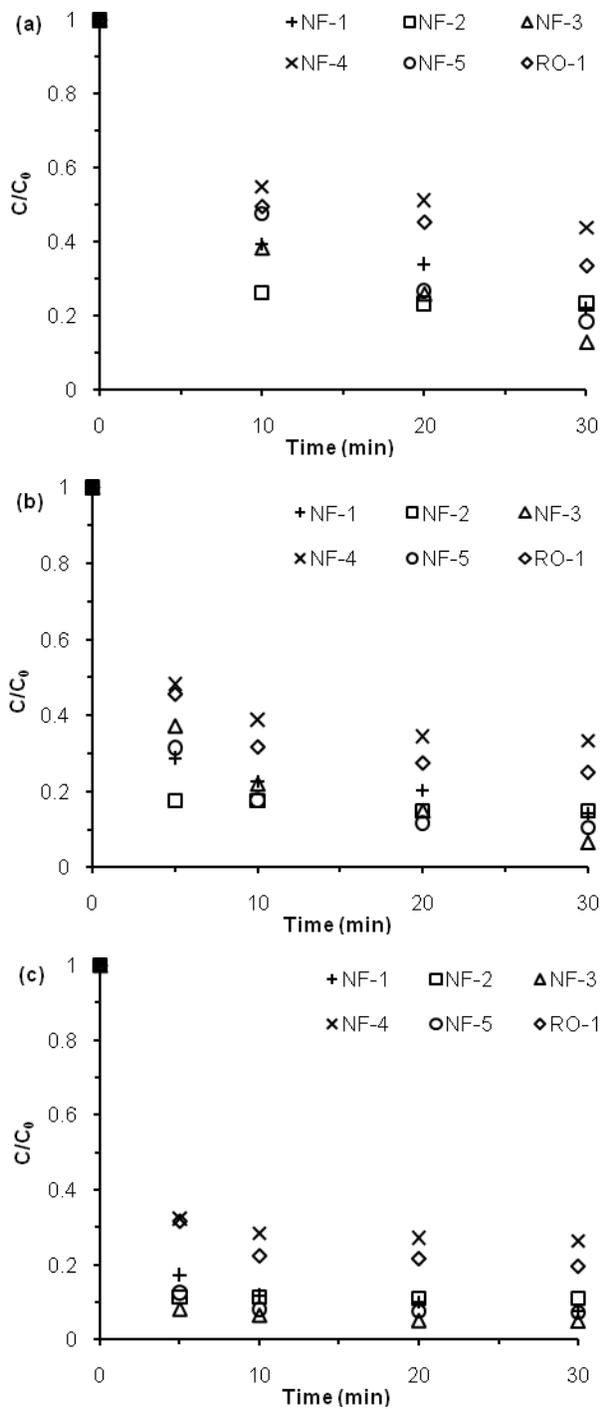


Figure 3-6. Rate of UV254 removal by MIEX-Cl resin at (a) 5 mL/L, (b) 10 mL/L, and (c) 20 mL/L.

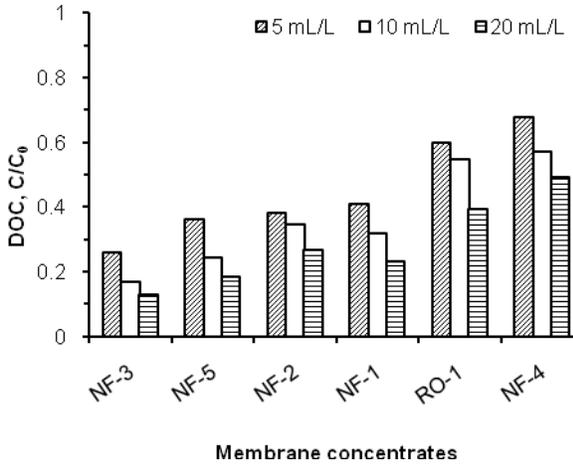


Figure 3-7. Effectiveness of MIEX-Cl resin for removal of DOC from membrane concentrate.

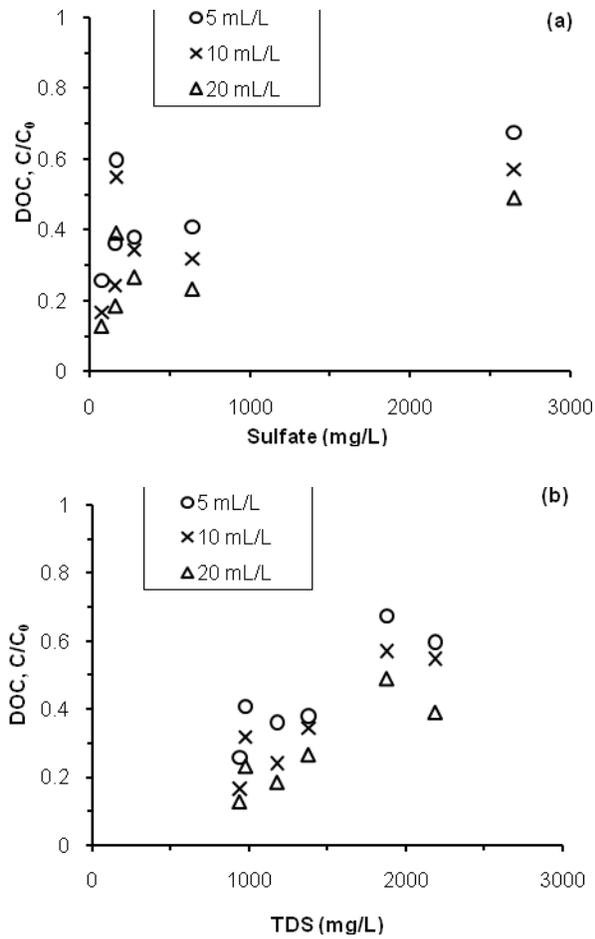


Figure 3-8. Effect of (a) sulfate and (b) TDS on DOC removal by MIEX-Cl treatment of membrane concentrate.

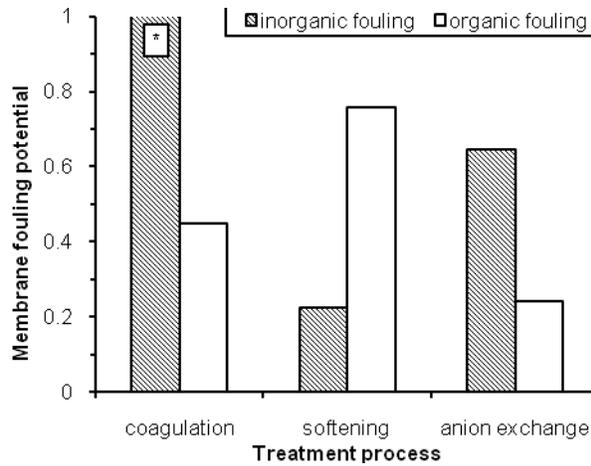


Figure 3-9. Effect of treatment on theoretical membrane fouling. Values <1 indicate reduction in membrane fouling. Data correspond to NF-5 membrane concentrate; coagulation (250 mg Fe(III)/L); softening (625 mg/L as CaO); anion exchange (10 mL/L MIEX-Cl resin). *Inorganic fouling potential for coagulation was 4.6.

CHAPTER 4 CONCLUSIONS AND RECOMMENDATIONS

Membrane treatment processes are a promising technology for treating alternative water sources including brackish, saline, and reclaimed water. However, membrane fouling and membrane concentrate production are two major obstacles to overcome when implementing membrane processes. Thus, a better understanding of reducing membrane fouling and managing membrane concentrate is needed. Various physical-chemical treatment processes were examined. Coagulation and lime softening were studied for membrane concentrate treatment. These treatment processes were not examined for groundwater treatment because they are already established in the drinking water industry. Cation exchange and combined ion exchange were examined for groundwater treatment. These treatment processes have not been well studied for groundwater or membrane concentrate treatment. Additionally, MIEX[®] treatment was studied for treatment of both groundwater and membrane concentrate.

For the majority of treatment scenarios described above, data for DOM (i.e. DOC and UV₂₅₄), divalent cations (i.e. total hardness), and divalent anions (i.e. sulfate) were collected. Thus, the following conclusions were made regarding combined ion exchange treatment of groundwater. With a 10× NaCl regenerant solution, the order of removal was: UV₂₅₄ > DOC > total hardness > sulfate > alkalinity. The single-use jar testing procedure may underestimate removal efficiency compared to the multiple loading procedure. Combined ion exchange achieved > 50% inorganic and organic fouling potential reduction. Thus, combined ion exchange can be an effective membrane pretreatment method. Combined ion exchange can be performed in one reactor, produces only one waste stream, and more efficiently uses the regenerant brine. In

regards to physical-chemical of membrane concentrate, the following conclusions were made. DOM properties and total hardness did not effect membrane concentrate treatment, but alkalinity and TDS did affect treatability. Physical-chemical treatment of membrane concentrate achieved > 50% reduction of either inorganic or organic fouling potential. Thus, combined treatment processes are needed to adequately reduce membrane fouling potential.

The following conclusions were made regarding physical-chemical treatment of different waters. In general, the order of DOC removal was: MIEX-Cl of membrane concentrate > coagulation > combined ion exchange > MIEX-Cl of groundwater > softening. A similar trend was observed for UV₂₅₄ removal: MIEX-Cl of membrane concentrate > coagulation ~ MIEX-Cl of groundwater > combined ion exchange > softening. For both types of water, various treatment processes were effective for DOM removal. Although the characteristics of these waters greatly vary, a common property of these waters is a high SUVA₂₅₄, which indicates that MIEX-Cl and coagulation will effectively remove DOM. The order of sulfate removal was: MIEX-Cl of membrane concentrate > MIEX-Cl of groundwater > combined ion exchange > softening. For both membrane concentrate and groundwater anion exchange treatment, DOM was preferentially removed compared to sulfate. In general, the order of removal for total hardness was: cation exchange > combined ion exchange > softening. By simplifying the order of removals of DOM and divalent cations, it is evident that these constituents are targeted by different treatment processes. As illustrated in Figure 2-9, combining treatment processes that remove both DOM and divalent cations results in the highest overall reduction of membrane fouling potential.

Thus, the following experiments are recommended for future work. Combined processes should be evaluated for the treatment of membrane concentrate: (i) anion exchange and softening, and (ii) anion exchange and cation exchange. Both combined processes would remove sulfate in addition to hardness and DOM, thus all components of membrane fouling potential as defined above would be reduced. Additionally, to fully analyze the efficiency of the proposed pretreatment and membrane concentrate treatment processes, bench-scale high-pressure membrane filtration should be tested. Proposed experiments include (i) nanofiltration of source water treated by combined ion exchange, (ii) nanofiltration of membrane concentrate treated by anion exchange and softening, and (iii) nanofiltration of membrane concentrate treated by combined ion exchange. Reverse osmosis membranes could also be used for bench-scale experiments. Performing bench-scale membrane filtration experiments will allow comparisons to be drawn between theoretical membrane fouling potential and membrane permeate flux rates.

To determine the feasibility of ion exchange treatment of membrane concentrate, a comparison of the volume of waste streams produced is needed. For example, ion exchange treatment of membrane concentrate would not be feasible if the volume of wastewater produced is greater than or equal to the volume of membrane concentrate produced by NF or RO treatment alone. Performing these additional experiments and feasibility studies will enhance high-pressure membrane filtration knowledge and technology. An increased understanding of the entire membrane filtration system is needed as alternative water sources become even more integrated within drinking water and industrial processes.

LIST OF REFERENCES

- Amokrane, A., Comel, C., Veron, J., 1997. Landfill leachates pretreatment by coagulation-flocculation. *Water Research* 31, 2775-2782.
- Apell, J.N., Boyer, T.H., 2010. Combined ion exchange treatment for removal of dissolved organic matter and hardness. *Water Research* 44, 2419-2430.
- Archer, A.D., Singer, P.C., 2006. An evaluation of the relationship between SUVA and NOM coagulation using the ICR database. *Journal American Water Works Association* 98, 110-123.
- Baek, S.O., Chang, I.S., 2009. Pretreatments to control membrane fouling in membrane filtration of secondary effluents. *Desalination* 244, 153-163.
- Boyer, T.H., Singer, P.C., 2005. Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors. *Water Research* 39, 1265-1276.
- Boyer, T.H., Singer, P.C., 2006. A pilot-scale evaluation of magnetic ion exchange treatment for removal of natural organic material and inorganic anions. *Water Research* 40, 2865-2876.
- Boyer, T.H., Singer, P.C., Aiken, G.R., 2008. Removal of dissolved organic matter by anion exchange: Effect of dissolved organic matter properties. *Environmental Science & Technology* 42, 7431-7437.
- Chelme-Ayala, P., Smith, D.W., El-Din, M.G., 2009. Membrane concentrate management options: a comprehensive critical review. *Canadian Journal of Civil Engineering* 36, 1107-1119.
- Choi, Y.J.K., Dempsey, B.A., 2004. In-line coagulation with low-pressure membrane filtration. *Water Research* 38, 4271-4281.
- Clesceri, L.S., Greenberg, A.E., Trussell, R.R., 1989. *Standard Methods for the Examination of Water and Wastewater*, 17th Edition ed. APHA.
- Cornelissen, E.R., Chasseriaud, D., Siegers, W.G., Beerendonk, E.F., van der Kooij, D., 2010. Effect of anionic fluidized ion exchange (FIX) pre-treatment on nanofiltration (NF) membrane fouling. *Water Research* 44, 3283-3293.
- Dialynas, E., Mantzavinos, D., Diamadopoulos, E., 2008. Advanced treatment of the reverse osmosis concentrate produced during reclamation of municipal wastewater. *Water Research* 42, 4603-4608.
- FDEP, 2007. *Tapping New Sources: Meeting 2025 water supply needs*, Annual Status Report on Regional Water Supply Planning.
http://www.dep.state.fl.us/water/waterpolicy/docs/RWSP_ASR_2006.pdf

- Gabelich, C.J., Williams, M.D., Rahardianto, A., Franklin, J.C., Cohen, Y., 2007. High-recovery reverse osmosis desalination using intermediate chemical demineralization. *Journal Membrane Science* 301, 131-141.
- Greenlee, L.F., Lawler, D.F., Freeman, B.D., Marrot, B., Moulin, P., 2009. Reverse osmosis desalination: Water sources, technology, and today's challenges. *Water Research* 43, 2317-2348.
- Greenlee, L.F., Testa, F., Lawler, D.F., Freeman, B.D., Moulin, P., 2010. Effect of antiscalants on precipitation of an RO concentrate: metals precipitated and particle characteristics for several water compositions. *Water Research* 44, 2672-2684.
- Heijman, S.G.J., Guo, H., Li, S., van Dijk, J.C., Wessels, L.P., 2009. Zero liquid discharge: Heading for 99% recovery in nanofiltration and reverse osmosis. *Desalination* 236, 357-362.
- Helferich, F., 1995. *Ion Exchange*. Dover Publications, New York. p 39-48.
- Hsu, S., Singer, P.C., 2009. Application of anion exchange to control NOM interference on lime softening. *Journal American Water Works Association* 101, 85-94,14.
- Hudson, N., Baker, A., Ward, D., Reynolds, D.M., Brunsdon, C., Carliell-Marquet, C., Browning, S., 2008. Can fluorescence spectrometry be used as a surrogate for the Biochemical Oxygen Demand (BOD) test in water quality assessment? An example from South West England. *Science of the Total Environment* 391, 149-158.
- Jarusutthirak, C., Mattaraj, S., Jiraratananon, R., 2007. Influence of inorganic scalants and natural organic matter on nanofiltration membrane fouling. *Journal Membrane Science* 287, 138-145.
- Lin, Y.P., Singer, P.C., Aiken, G.R., 2005. Inhibition of calcite precipitation by natural organic material: Kinetics, mechanism, and thermodynamics. *Environmental Science & Technology* 39, 6420-6428.
- Mobed, J.J., Hemmingsen, S.L., Autry, J.L., McGown, L.B., 1996. Fluorescence characterization of IHSS humic substances: Total luminescence spectra with absorbance correction. *Environmental Science & Technology* 30, 3061-3065.
- Mohammadesmaeili, F., Badr, M.K., Abbaszadegan, M., Fox, P., 2010. Byproduct Recovery from Reclaimed Water Reverse Osmosis Concentrate Using Lime and Soda-Ash Treatment. *Water Environment Research* 82, 342-350.
- Ning, R.Y., Troyer, T.L., 2009. Tandem reverse osmosis process for zero-liquid discharge. *Desalination* 237, 238-242.

- Qu, D., Wang, J., Wang, L.L., Hou, D.Y., Luan, Z.K., Wang, B.Q., 2009. Integration of accelerated precipitation softening with membrane distillation for high-recovery desalination of primary reverse osmosis concentrate. *Separation and Purification Technology* 67, 21-25.
- Renou, S., Poulain, S., Givaudan, J.G., Moulin, P., 2008. Treatment process adapted to stabilized leachates: Lime precipitation-pretreatment-reverse osmosis. *Journal Membrane Science* 313, 9-22.
- Russell, C.G., Lawler, D.F., Speitel, G.E., 2009. NOM coprecipitation with solids formed during softening. *Journal American Water Works Association* 101, 112-124.
- Shih, W.Y., Rahardianto, A., Lee, R.W., Cohen, Y., 2005. Morphometric characterization of calcium sulfate dihydrate (gypsum) scale on reverse osmosis membranes. *Journal Membrane Science* 252, 253-263.
- SJRWMD, 2006. District Water Supply Plan 2005, Palatka, Florida. Technical Publication SJ2006-2. <http://www.sjrwmd.org/technicalreports/pdfs/TP/SJ2006-2.pdf>
- Sperlich, A., Warschke, D., Wegmann, C., Ernst, M., Jekel, M., 2010. Treatment of membrane concentrates: phosphate removal and reduction of scaling potential. *Water Science & Technology* 61, 301-306.
- Squire, D., 2000. Reverse osmosis concentrate disposal in the UK. *Desalination* 132, 47-54.
- Tatsi, A.A., Zouboulis, A.I., Matis, K.A., Samaras, P., 2003. Coagulation-flocculation pretreatment of sanitary landfill leachates. *Chemosphere* 53, 737-744.
- Thompson, J.D., White, M.C., Harrington, G.W., Singer, P.C., 1997. Enhanced softening: Factors in influencing DBP precursor removal. *Journal American Water Works Association* 89, 94-105.
- U.S. Census Bureau, P.D., 2004. Table 6: Total populations for regions, divisions, and states: 2000 to 2030.
- Van der Bruggen, B., Lejon, L., Vandecasteele, C., 2003. Reuse, treatment, and discharge of the concentrate of pressure-driven membrane processes. *Environmental Science & Technology* 37, 3733-3738.
- Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science & Technology* 37, 4702-4708.

BIOGRAPHICAL SKETCH

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