OPTIMIZING A HYBRID REVERSE OSMOSIS/ELECTRODIALYSIS SYSTEM FOR NATURAL ORGANIC MATTER CONCENTRATION

BY

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THESIS

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ABSTRACT

Reverse osmosis (RO) and electrodialysis (ED) were examined to determine an optimum way to concentrate natural organic matter (NOM) for chemical and biological characterization of disinfection by-products (DBPs). RO is an effective way to concentrate NOM. However, it also concentrates inorganic ions which lead to an increase in the osmotic pressure, eventually rendering RO ineffective, and potentially producing membrane scaling. Salts are also harmful to mammalian cells at high concentrations, which may cause artifacts in the toxicological outcomes. Thus ED was introduced to remove the inorganic ions. However, since a portion of NOM is negatively charged, it is not retained well by ED.

Due to the ion exchange properties of ED membranes, sodium sulfate and sodium chloride were added at different time points and amounts in order to optimize the retention and concentration of NOM. It was found that a high concentration of sodium chloride displaced NOM that had adsorbed to anion exchange sites on the membranes, and was able to prevent loss of NOM. However, calcium was removed slowly due to the high sodium concentration, which limited the amount of sulfate that could be added. Meanwhile, continually adding sulfate at lower concentrations (low enough to prevent calcium sulfate precipitation) resulted in an initial loss of NOM, but eventually no further loss occurred as sulfate took over the anion exchange sites. However, not all of the calcium could be removed this way, and the presence of limited sulfate makes it infeasible to achieve large concentration factors. In order to optimize this process, calcium should be removed prior to concentration.

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CHAPTER 1: INTRODUCTION

1.1 Motivation

Natural organic matter (NOM) is present in surface and ground waters, and comes from the decay of plants and animals in the environment. NOM does not have a unique structure and is difficult to characterize and isolate. NOM is not harmful, but when combined with chlorine or other disinfectants, reactions take place that produce disinfection by-products (DBPs), including some that are potentially harmful.

Due to regulations in the Stage 2 Disinfectants/DBP Rule and the Long-Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR), many water utilities are switching from using free chlorine to combined chlorine for residual disinfection, as combined chlorine produces fewer of the regulated DBPs. However, combined chlorine can produce nitrogen-containing DBPs (N-DBPs) and iodinated DBPs (I-DBPs), which have been shown to have a higher mammalian cytotoxicity and genotoxicity than the regulated DBPs (Richardson et al., 2007). Besides the use of disinfectant, utilities must also begin to consider whether to repair aging distribution systems or convert traditional systems to dual systems. Changes in the system could result in changes in the hydraulic residence time, which could in turn lead to differences in microbial growth as well as in DBP formation.

While the toxicity of many individual DBPs has been determined (Plewa et al., 2010), some DBPs are not stable and undergo reactions depending on the contact time and type of disinfectant used. Therefore, the overall toxicity of a DBP mixture would be more relevant to assess when determining the best disinfectant and contact time to select. In order to obtain a meaningful toxicity response, a highly concentrated DBP sample is desired. This can be done by either first disinfecting and then concentrating the resulting solution (which could result in loss of DBPs by volatilization or permeation through membranes), or pre-concentrating NOM and then adding disinfectant (higher contact time and/or disinfectant concentration differ from real conditions). The latter method will be used so as not to lose the volatile DBPs.

1.2 Objectives

A new way to concentrate NOM (to which different disinfection schemes will be applied) using a hybrid reverse osmosis/electrodialysis (RO/ED) system will be explored here. If effective, this system will be able to concentrate large volumes of water while retaining most of the NOM and keeping the concentration of salts low. The hybrid RO/ED system will be optimized to concentrate NOM for whole mixture DBP studies. The main goals will be to examine the ion exchange properties of ED and to utilize these findings to minimize total organic carbon (TOC) loss.

CHAPTER 2: LITERATURE REVIEW

2.1 Previous Concentration Methods

The concentration of natural organic matter for disinfection by-product (DBP) studies has been explored by the U.S. EPA (Speth et al., 2008; Simmons et al., 2008). The goal of the study was to determine the *in vitro* and *in vivo* health effects of complex mixtures of DBPs that would be representative of what is found in most distribution systems. The research team of this study decided to concentrate finished drinking water, and spike back the DBPs lost in the concentration process. They were able to achieve a concentration factor of 136 times for chlorinated samples and 124 times for ozonated/postchlorinated samples by passing the waters through hydrogen-form cation-exchange resin columns to remove hardness and quench free chlorine, and then concentrating with reverse osmosis membranes. With this method, the final pH of the concentrates were 1.6 and 1.5 for chlorinated and ozonated/postchlorinated waters, respectively, and sodium hydroxide had to be added to adjust the pH back to 7 in order to minimize the potential for structural changes in the organics. They were able to recover 86% and 84% TOC and 68% and 62% total organic halide (TOX) before spike-back for the chlorination and ozonation/postchlorination waters, respectively. The positively charged DBPs could have been retained on the hydrogen-form cation-exchange resin, while smaller, neutral DBPs could have permeated through the reverse osmosis membrane. Also, structural changes due to low pH could have irreversibly altered the DBPs. Finally, biological degradation could have occurred as well. Despite concentrating the waters over 100 times, they were not able to see a measurable effect *in vivo* (Narotsky et al., 2008), which indicates that a higher concentration factor is necessary.

Another concentration method that has been used is XAD extraction, where compounds adsorb onto the surface of the resin, and then are extracted using an appropriate solvent. XAD resins are nonionic macroporous copolymers that can differ in pore size, surface area, and polarity (Aiken, 1988). XAD resins isolate selected fractions of NOM, but certain portions will adsorb irreversibly, and will thus be lost in the process. However, XAD will retain NOM without retaining inorganic ions. XAD extraction was not a favorable method for the animal toxicological study because large volumes of water were needed and had to be in aqueous form (Simmons et al., 2002; Simmons et al., 2008).

Reverse osmosis is the most effective way to recover NOM, with a median recovery of ~90% (Perdue and Ritchie, 2003). Unfortunately, RO also concentrates inorganic ions, and is often coupled with a cation-exchange resin to remove hardness such as calcium and magnesium, which if concentrated could lead to scaling of the membrane surface by sparingly soluble salts. Sulfate and dissolved silica tend to remain in the RO concentrate. The percent recovery of NOM by membrane processes is strongly dependent on the rejection and the water concentration factor. The relationship is shown in Equation 2.1 (Perdue and Ritchie, 2003):

$$Percent\ recovery = \frac{100}{W(1-R)}\{1 - R \cdot \exp([-(1-R)(W-1)])\} \qquad \text{Equation 2.1}$$

where W = water concentration factor

R = rejection.

If the sample is concentrated too much or the rejection is too low, the percent recovery will be lower. Figure 2.1 shows how the percent recovery will decrease as the water concentration factor increases and at rejections of R = 0.995 and R = 0.99.

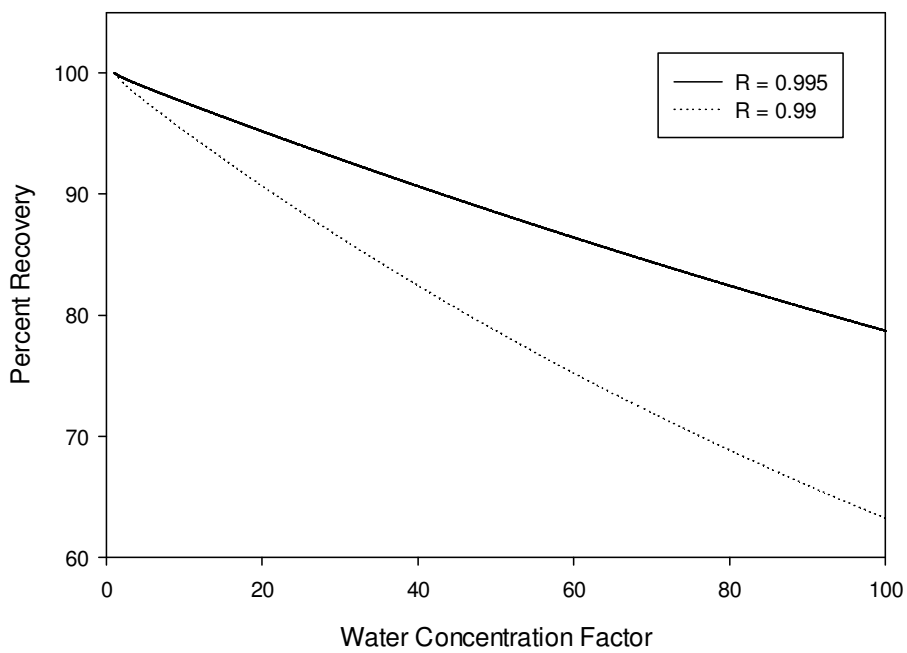


Figure 2.1: Percent recovery of NOM vs. Water concentration factor in reverse osmosis at rejections of 0.995 and 0.99.

A combined approach to concentrating natural organic matter was used by a group of researchers at Georgia Institute of Technology and Kansas State University (Koprivnjak et al., 2006; Vetter et al., 2007; Gurtler et al., 2008). They coupled reverse osmosis with electrodialysis in order to concentrate NOM without building up a high concentration of inorganic solutes. Studies were done on both fresh waters and seawater.

In the freshwater study (Koprivnjak et al., 2006), the emphasis was placed on removing sulfate and silicic acid, as the cations were removed by an hydrogen-form cation exchange resin, and anions that produced relatively volatile acids were removed during the freeze drying process. Sulfate and silicic acid interfere with estimations of phenolic and carboxylic contents of NOM, and are undesirable for their goal to characterize NOM. At their optimal conditions, using a 5 cell pair ED stack, they were able to remove 79% of sulfate, 65% of silicic acid, while recovering 102% of TOC. In their other experiments, they speculated that most of the TOC was lost by adsorption to the membranes, with most of the loss occurring within the first hour. However, they still achieved good TOC recovery, with an average recovery of 84%.

The same group of researchers used RO and ED to concentrate dissolved organic matter (DOM) in seawater (Vetter et al., 2007). They were able to recover 64-93% of DOC by running an initial ED phase to remove salts, followed by an RO/ED phase to remove both water and salts, and a final ED phase to reduce the conductivity to around 10 mS/cm. They found that most of the DOC was lost in the final ED phase. During this phase, there were fewer inorganic anions to carry the electrical current as well as to adsorb to the anion exchange sites. Gurtler et al. (2008) found that by pulsing the electrical current, they were able to obtain a higher recovery of DOM. They used a pulse frequency of 0.25 Hz, with a similar protocol: initial ED phase to remove salts, RO/ED phase to reach target volume, and final ED phase with pulsed ED. Using this protocol, they achieved high recovery of DOM until a conductivity of 1 mS/cm was reached. They hypothesized that pulsing created a “relaxation time” that prevents fouling by allowing a re-mixing of the boundary layer, which has been depleted of the faster diffusing inorganic anions.

Ions are depleted at the membrane surface in the diluate compartment due to concentration polarization. Concentration polarization is caused by the difference in ion transfer numbers

between the solution and the membranes. This lowers the limiting current, increases cell resistance, and restricts the ED capacity. Pulsing was investigated to try to decrease the concentration polarization that occurs in ED (Mishchuck et al., 2001). Concentration polarization could be mitigated by making the duration of the current or voltage pulses shorter than the characteristic time to build up the polarization layer. The pulse-pause duration ratio and the pulse frequency were important parameters in the optimization of the salt removal.

Lee et al. (2002) examined pulsed ED as a way to reduce fouling of humate on ED membranes. However, they found that a pulsing frequency of 100 Hz was most effective at reducing fouling, and at other frequencies cell resistance increased before the salts were depleted, indicating that the membranes were being fouled. They proposed that pulsing caused increasing mixing effects in the boundary layer, which disturbed the formation of the gel layer on the surface of membranes.

2.2 Electrodialysis as a Selective Process

Electrodialysis is a membrane process that uses an applied potential and alternating positively and negatively charged ion exchange membranes to transfer charged molecules from between solutions (Figure 2.2). It is more desirable to remove certain ions from the feed water than others, and the ability of ED to selectively remove certain species has been examined.

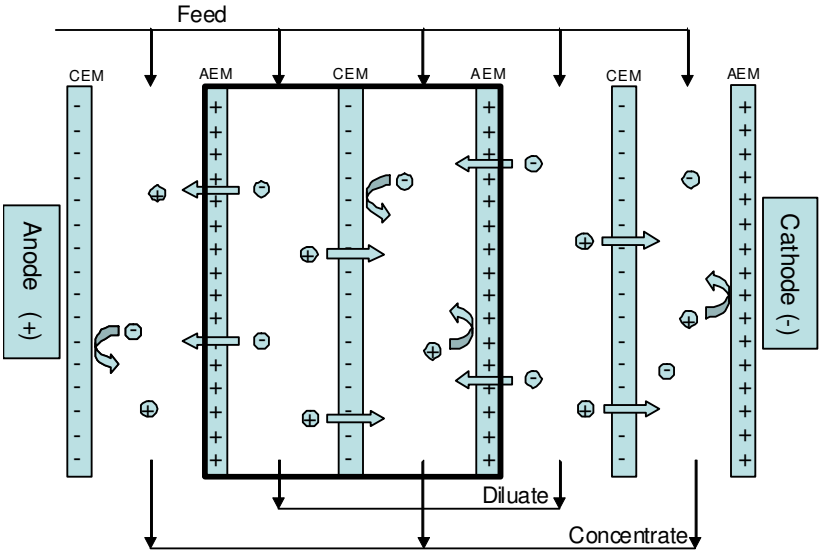


Figure 2.2: ED consists of alternating cation exchange membranes (CEM) and anion exchange membranes (AEM) with an applied voltage.

Van der Bruggen et al. (2004) explored the separation of monovalent and divalent ions using ED. They used two types of ion exchange membranes: conventional, nonselective membranes and monovalent-selective ion exchange membranes. With the nonselective membranes, NaCl was transported the fastest, while $MgSO_4$ was removed the slowest. Multivalent ions are more strongly retained in the membrane and more sterically hindered, so they are transported more slowly. Use of the selective membranes resulted in greater separation efficiencies, although the fraction of ions removed was lower, as they faced a larger resistance against mass transport. The separation efficiency also depended on the charge of the counterion. If separation between magnesium and sodium was desired, it would be more effective with chloride as the counterion instead of sulfate. Sulfate, as the divalent counterion, would be transported more slowly, which would result in a slower transport of the co-ions (magnesium or sodium) to keep the charge balance. This is less favorable for monovalent ions, and thus the separation efficiency is decreased.

Zhang et al. (2011) have investigated the separation of small organic ions and salts using ED. They used a synthetic feed solution composed of NaCl, $MgSO_4$, $NaNO_3$, $NaHCO_3$, and Na_2HPO_4 with 120 mg/L of an organic ion (formate, acetate, propionate, butyrate, tartrate, or aspartate). They found that chloride and sulfate ions were transported much faster than acetate, propionate, and butyrate, and these were removed appreciably only after the inorganic anions were removed. Formate and aspartate were removed at about the same rate throughout the experiment. Tartrate, which has a net charge of –2 at the pH tested and is highly hydrophilic, did not behave differently from chloride and sulfate, and there was no selectivity between them. They also hypothesized that since aspartate and tartrate had ionic sizes comparable to the free volume size of the anion exchange membrane, these molecules adsorbed to the surface, forming a double layer structure, which repulsed sulfate more than chloride. This was their explanation for why sulfate ion flux was not increased for experiments at higher voltage.

2.3 Ion Exchange Properties of Electrodialysis Membranes

Ion exchange membranes are made up of ionic groups attached to a polymer matrix. The focus of this section will be on anion-exchange membranes, as natural organic matter tends to be negatively charged, and negatively charge foulants only affect the anion exchange membrane

(Lindstrand et al., 2000a; Lindstrand et al., 2000b). Anion-exchange membranes contain positively charged groups, such as $-NH_3^+$, $-NRH_2^+$, $-NR_2H^+$, $-NR_3^+$, $-PR_3^+$, and $-SR_2^+$ (Xu, 2005). The quaternary amine is the strongest anion-exchange resin, followed by the ternary, secondary, and primary amine. In monovalent/divalent exchange, the isotherms will change depending on total ion concentration in the aqueous phase. At low concentrations, the membrane will prefer the ion with the higher valency. The selectivity constant could change if resin swelling occurs.

Boari et al. (1974) did a theoretical analysis and found the following selectivity sequence towards the sulfate ion with respect to the chloride ion: primary amino group > secondary group > tertiary group > quaternary group resin. This shows the increasing predominance of the electrostatic (net point charge, dipole moment) interactions over the hydrostatic (involving the break up of the hydrated structure) interactions (Boari et al., 1974).

Ion exchange selectivity at equilibrium depends on the selectivity constant and in case of a monvalenet/divalent exchange also on the total concentration of ions in solution and the ion exchange capacity of the resin. The equilibrium isotherms describing the selectivity for monovalent-divalent exchange, illustrated with Cl^- and $SO_4^=$, is:

$$\frac{y_{SO_4}}{(1-y_{SO_4})^2} = \frac{x_{SO_4}}{(1-x_{SO_4})^2} K_{Cl}^{SO_4} \frac{\overline{C}}{C} \qquad \text{Equation 2.2}$$

Where $\overline{C}$ = capacity of anion exchange membrane (eq/L)

C = total aqueous ion concentration (eq/L)

y_{SO_4} = equivalent fraction of $SO_4^=$ in the anion exchange membrane

x_{SO_4} = equivalent fraction of $SO_4^=$ in solution

$K_{Cl}^{SO_4}$ = selectivity coefficient for $SO_4^=$ exchanging with Cl^- onto membrane

In the case of monovalent-monovalent exchange, the isotherm has a simpler form, illustrated with Cl^- and a generic monovalent NOM ion, NOM^-:

$$\frac{y_{NOM}}{(1-y_{NOM})} = \frac{x_{NOM}}{(1-x_{NOM})} K_{Cl}^{NOM} \qquad \text{Equation 2.3}$$

Where y_{NOM} = equivalent fraction of NOM^- in the anion exchange membrane

x_{NOM} = equivalent fraction of NOM^- in solution

K_{Cl}^{NOM} = selectivity coefficient for NOM^- exchanging with Cl^- onto the membrane

Figure 2.3 shows the isotherms for a chloride-to-sulfate selectivity coefficient $K_{Cl}^{SO_4} = 0.1$. These curves show how the fraction of sites taken up by sulfate and chloride in the membrane changes with aqueous fraction and total concentration. At low concentrations it is seen that the membrane prefers sulfate over chloride, even if the selectivity for sulfate is low. For monovalent-monovalent exchange, possible isotherms for different selectivity constants are shown in Figure 2.4.

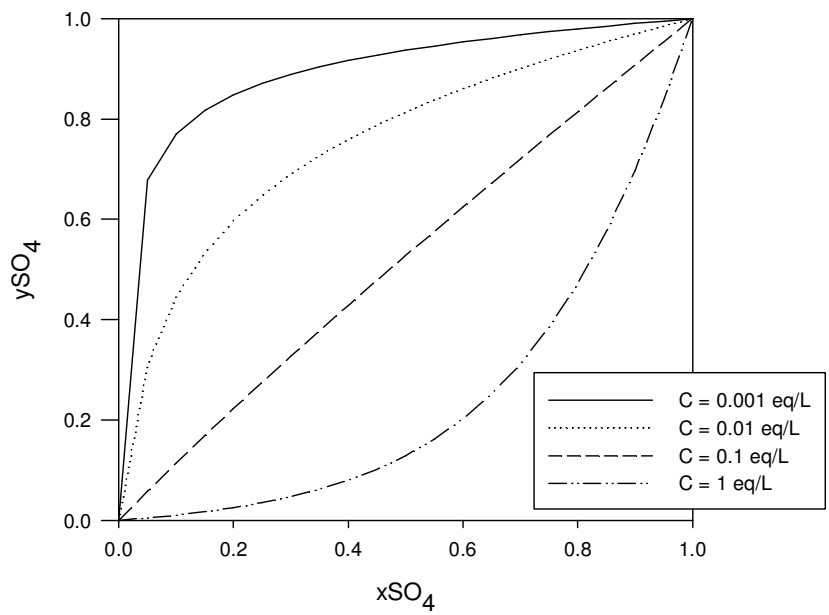


Figure 2.3: Anion exchange isotherm in the presence of sulfate and chloride for a chloride-to-sulfate selectivity $K_{Cl}^{SO_4}$ =0.1, which was roughly determined from experimental data. x_{SO4} is the aqueous equivalent fraction of sulfate, whereas y_{SO4} is the equivalent fraction of anion exchange sites occupied by sulfate.

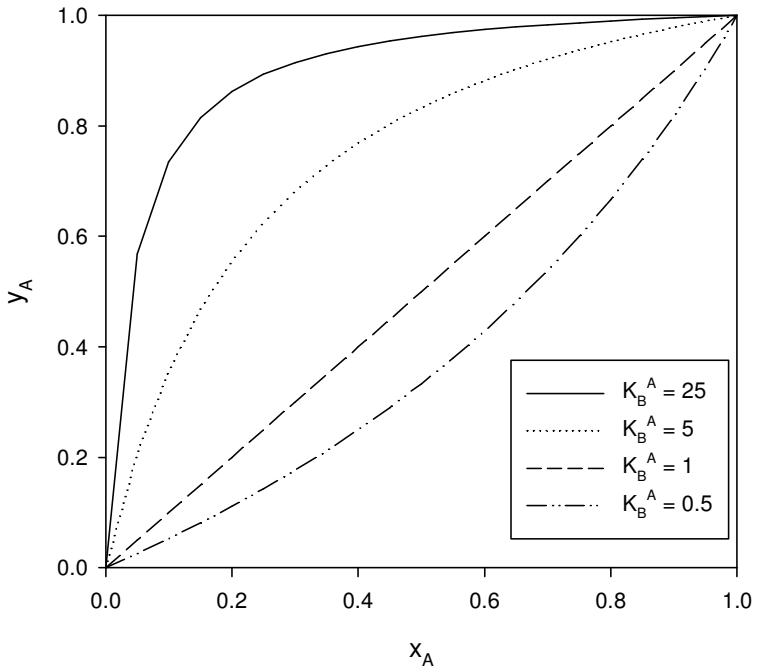


Figure 2.4: Ion exchange isotherm for monovalent-monovalent exchange. x_A is the fraction of solute A in the aqueous phase, whereas y_A is the fraction of ion exchange sites taken up by solute A.

In monovalent-monovalent ion exchange, the total concentration in the aqueous phase does not change the properties of the isotherm. For the exchange of organics for chloride, if the selectivity for organics is high, then a high concentration of chloride must be added to minimize TOC loss.

CHAPTER 3: MATERIALS AND METHODS

3.1 Reverse Osmosis Membrane and Setup

A Dow Filmtec TW30-2514 membrane (The Dow Chemical Company, Midland, MI) was used in the reverse osmosis system. The characteristics of the membrane, given by the manufacturer, are listed in Table 3.1.

Table 3.1: Dow TW30-2514 membrane characteristics

Size	2.5 in. x 14 in.
Nominal active surface area	0.7 m^2
Permeate flow rate*	0.53 L/min
Stabilized salt rejection*	99.5%

*Based on 2000 ppm NaCl, 225 psig, and 5% recovery

This membrane was chosen because of its use in previous efforts to concentrate NOM (Koprivnjak et al., 2006; Gurtler et al., 2008; Vetter et al., 2007), and because it was readily available. The 2.5 inch size was chosen because the pump available (CAT pump 341) constrained the feed flow rate to less than 15 L/min.

The membrane was housed in a 316SS pressure vessel (Applied Membranes). A diaphragm pressure regulator (Equilibar, Fletcher, NC) was installed at the concentrate outlet to control the pressure. A VWR Recirulator recirculated water at 18 $^{\circ}$C through a stainless steel coil in the feed tank.

3.2 Electrodialysis Setup

A 30-cell pair Mk I ED stack (GE Power & Water, Westborough, MA) was used with AR204SZRA anion and CR67HMR cation exchange membranes. Characteristics of the ion exchange membranes are listed in Table 3.2.

Table 3.2: Characteristics of GE ion exchange membranes

	AR204SZRA anion exchange membrane	CR67HMR cation exchange membrane
Thickness (mm)	0.55-0.60	0.60-0.65
Active membrane area (cm^2)	280	280
Initial membrane resistance (ohm-cm^2)	7-8	9-11
Capacity (eq/L)	1.18	1.08
Functional group	Quaternary ammonium ions	Sulfonate groups

The ED stack was connected to an Ametek DCS 100-10E (100 V, 10 A) power supply. For pulsed experiments, the power supply was connected to a solid state relay, which was controlled by a pulse generator (Philips PM 5715). The frequency of the pulse was set to 0.7 Hz. Three Fluid-o-Tech MG200 series gear pumps (MG213XD1P-C52VS) were used to pump the diluate, concentrate, and electrolyte solutions from their respective tanks. The flow rates of each stream were controlled using WEG CFW10 inverters. The diluate stream was run in batch, while the concentrate stream was either recirculated or run continuously, depending on the experiment.

3.3 Reagents

General laboratory reagents were purchased from Fisher Scientific (Fair Lawn, NJ) and Sigma-Aldrich Company (St. Louis, MO).

3.4 Analytical Techniques

Concentrations of sulfate and chloride ions were measured by ion chromatography (ICS-2000, Dionex, Sunnyvale, CA) using a Dionex IonPac AS19 column. Total organic carbon was measured using a Shimadzu TOC-VCPH TOC analyzer. A spectrofluorometer (Shimadzu RF-5301PC) was used to measure fluorescence in order to determine Rhodamine WT rejection. Size exclusion chromatography was performed using a PL aquagel-OH Analytical column (Agilent Technologies, Santa Clara, CA) and a Waters Alliance HPLC (Waters e2695 Separation Module) with a UV detector (Waters 2489 UV/Visible Detector). Calcium was measured by the USEPA Standard EDTA Titrimetric Method using a Hach Digital Titrator with CalVer 2 Calcium Indicator Powder Pillows and 0.0800 M EDTA.

3.5 Characterization of Reverse Osmosis Membrane

The performance of the reverse osmosis membrane was characterized by testing NaCl and Rhodamine WT (RWT) solutions. The feed was composed of 20 L of deionized water, and a single solute at a concentration of either 1 or 2 g/L NaCl, and 2.5 mg/L RWT. The RO system was run in batch recirculation, with permeate and reject streams being returned to the feed tank.

3.6 Characterization of Electrodialysis Stack

To characterize the ED stack, 2 g/L NaCl was added to the diluate tank, the concentrate tank was filled with deionized water, and the electrolyte tank was made up of a solution of 0.7% Na_2SO_4. All three tanks were run in batch recirculation, and different experiments were run with a flow rate of 0.5 L/min, 1.5 L/min, and 1.5 L/min with pulsed ED. The conductivity of each stream was monitored by a Cole-Parmer 100-Ohm Pt RTD Conductivity Cell.

3.7 Summary of Experimental Protocols

The experiments performed were designed based on the results obtained for each previous experiment. In total, 14 experiments were run to troubleshoot and optimize the proposed RO/ED system. Figure 3.1 shows the experimental setup, while Figure 3.2 shows the progression and summary of the experiments performed.

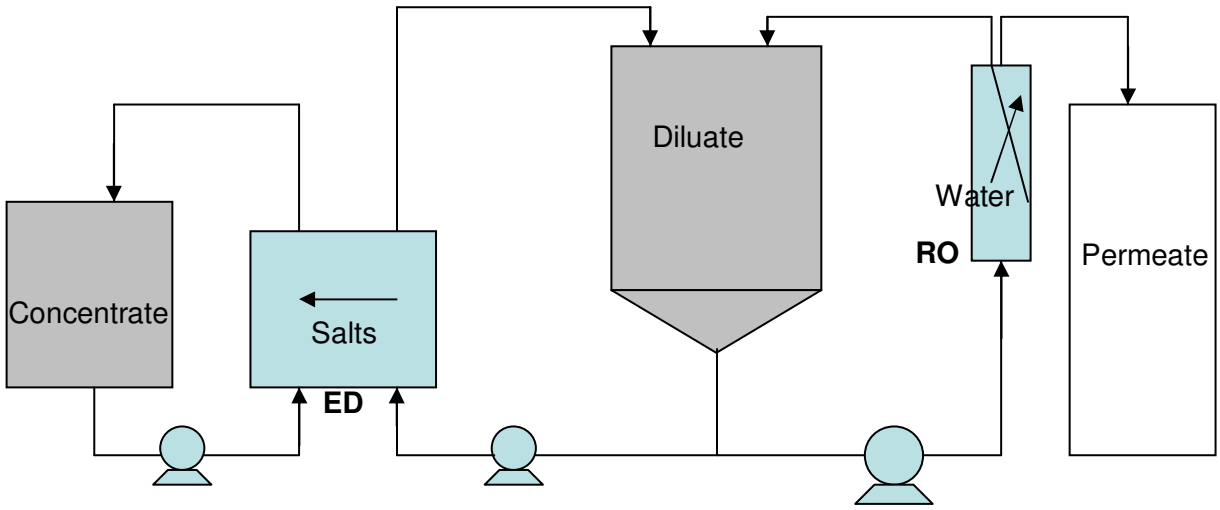


Figure 3.1: Hybrid RO/ED system.

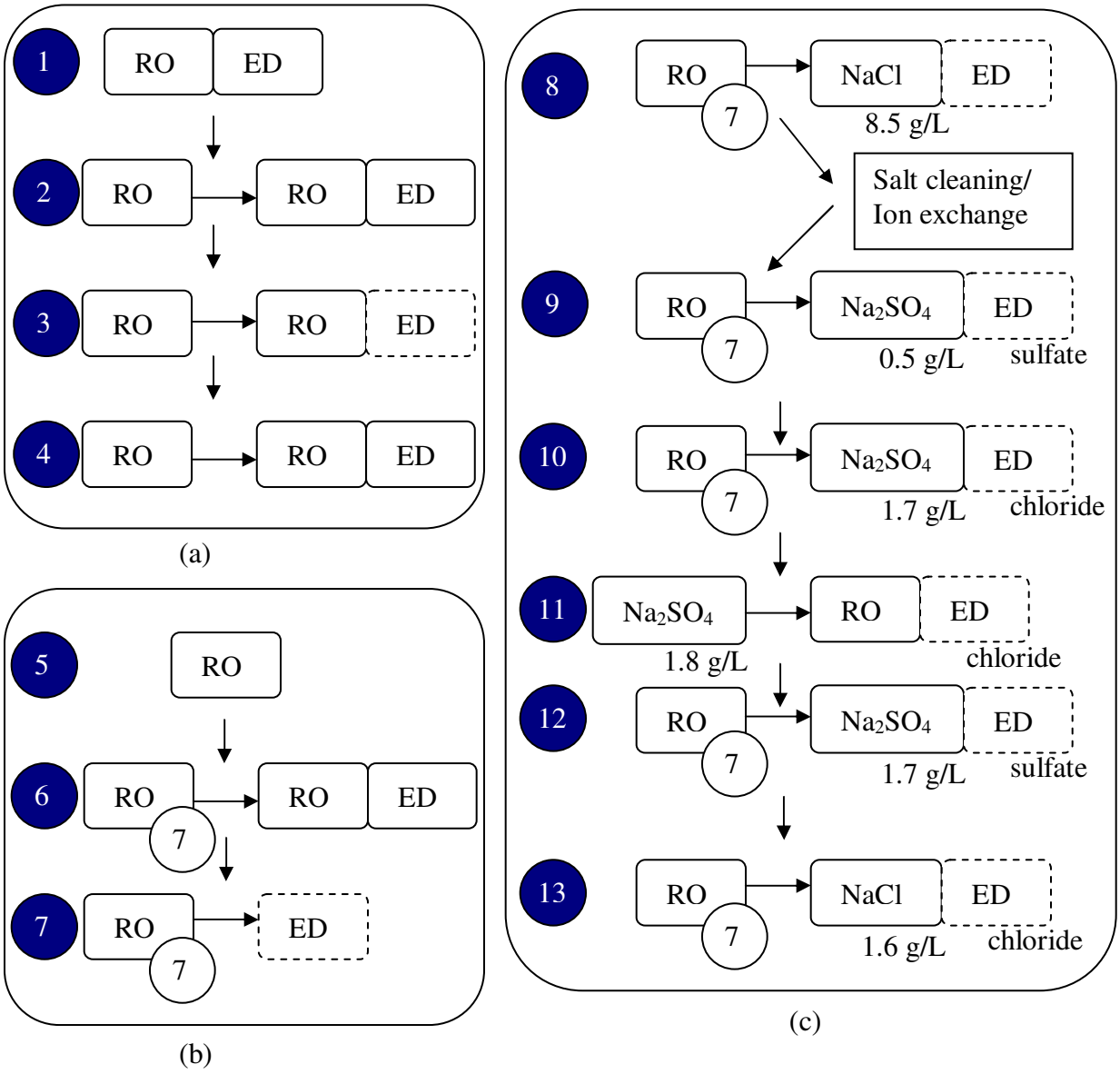
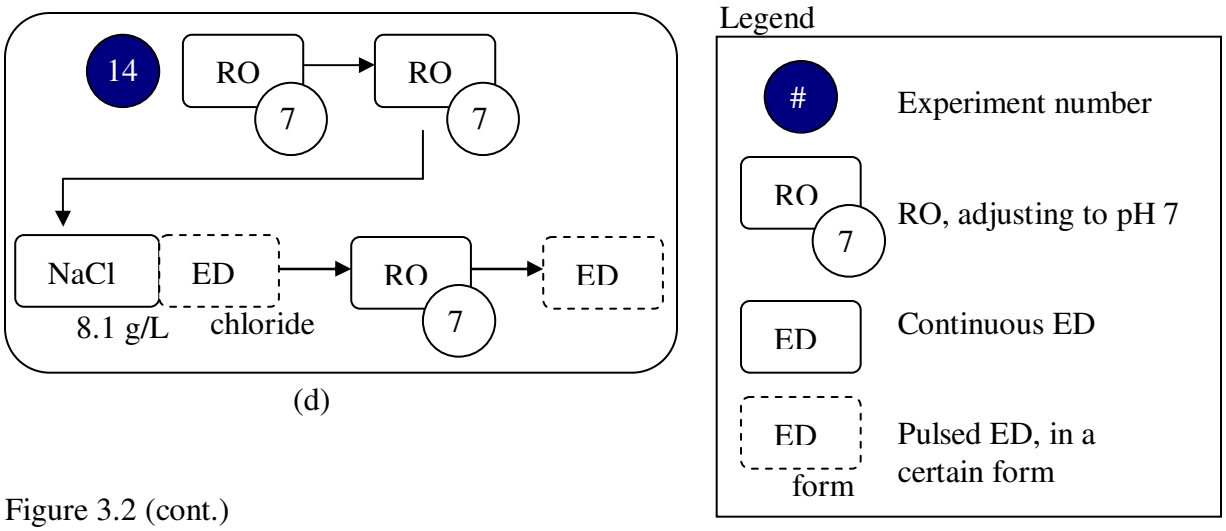


Figure 3.2: Experimental protocols for: (a) Preliminary RO/ED experiments; (b) Isolating TOC loss experiments; (c) Tap water with salt addition experiments; and (d) Final concentration experiment.



(d)

Figure 3.2 (cont.)

3.8 Tap Water Experiments

Experiments to concentrate NOM were run using tap water, as the NOM here would be representative of that found in treated waters. Tap water was added to the diluate tank, with an excess of sodium bisulfite added to quench the residual chlorine to prevent it from damaging the RO membrane. In later experiments, the tap water was first run through a 10µm and a 1µm filter in series to remove small particles.

3.8.1 Preliminary RO/ED Experiments

Preliminary RO/ED experiments (Figure 3.2a) were run to see if the concentration methods proposed by Gurtler et al. (2008) and Koprivnjak et al. (2006) would be effective to concentrate the NOM in tap water. In these experiments, RO was run and ED was introduced at different times during the process.

3.8.2 Isolating TOC Loss

Since TOC loss was observed in the preliminary RO/ED experiments, RO and ED were isolated to determine the point in the process that TOC loss was occurring (Figure 3.2b).

3.9 Ion Exchange Experiments

In an effort to see if a high conductivity would retain TOC, NaCl was added at 8.5 g/L to water that was previously concentrated five times by RO. Next, cleaning experiments were performed by exposing the membranes to high concentrations of sodium chloride. Experiments exploring the selectivity of the anion exchange membranes were also conducted.

3.9.1 Salt Cleaning

A total of 8 batches of water were run through both the ED diluate and concentrate streams, with no applied voltage. Initial batches consisted of 10 g/L NaCl. Later cleaning experiments were performed by using a solution of 30 g/L NaCl, and incrementally increasing the concentration by 10 g/L until the solution was 70 g/L NaCl. After each addition, the streams were circulated for 2 hours to allow the membranes to reach equilibrium.

3.9.2 Determining Sulfate vs. Chloride Selectivity

After running 60 and 70 g/L NaCl through the ED stack, it was assumed that the anion exchange membranes were in chloride form. Deionized water was run through the stack to rinse the membranes, and afterwards, a 4 g/L Na_2SO_4 solution was run through both the diluate and concentrate streams. Later 1 g/L Na_2SO_4 was added to both the diluate and concentrate tanks and circulated for 2 hours.

3.10 Tap Water with Salt Addition Experiments

To examine the effects of salt addition, RO was used to concentrate the tap water approximately 5 times, and varying amounts of sodium chloride or sodium sulfate were added to the diluate water prior to running ED (Figure 3.2c).

3.10.1 ED with Sulfate Addition

Due to the behavior of monovalent-divalent exchange, which prefers the divalent ion at low concentrations (Figure 2.3), sodium sulfate was added to concentrated RO water prior to running ED. Two concentrations of Na_2SO_4 were tested: 0.5 g/L and 1.7 g/L. The concentration of 1.7 g/L was tested both with the anion exchange membranes being in either the chloride form or sulfate form. Sodium sulfate was added throughout the ED experiment to keep the conductivity

constant. For an initial addition of 1.7 g/L, a total of 18.92 g Na_2SO_4 was added throughout 4.5 hours for the experiment done in chloride form, while a total of 10.87 g Na_2SO_4 was added within 4 hours for the experiment in sulfate form. Another experiment that was tried was adding 1.8 g/L Na_2SO_4 prior to concentration, and then running RO and ED simultaneously with no subsequent salt addition.

3.10.2 ED with Chloride Addition

In order to compare the effectiveness of sulfate versus chloride in retaining NOM in ED, sodium chloride was added to concentrated RO water prior to running ED. In this experiment, 1.6 g/L NaCl was added, and throughout the next 4 hours, 31 g NaCl was added to keep the conductivity constant.

3.10.3 Final Concentration Experiment

A final concentration experiment was run to see if RO coupled with ED and salt addition could be used to produce a concentrated sample of NOM (Figure 3.2d). In this experiment, RO was used to concentrate 118 L to 13 L, and the tank was refilled to 119 L and concentrated to 20 L. Then 160 g NaCl was added to this 20 L, and run through ED for 4 hours to remove calcium. NaCl was continuously added to keep the conductivity constant. The tank was then refilled to 118 L and concentrated to 15 L using RO. This 15 L was run through ED for 4 hours. No further salt was added during this second ED run.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characterization of Reverse Osmosis Membrane

The RO membrane was characterized using both NaCl and RWT. The amount of passage vs. pressure is shown in Figure 4.1.

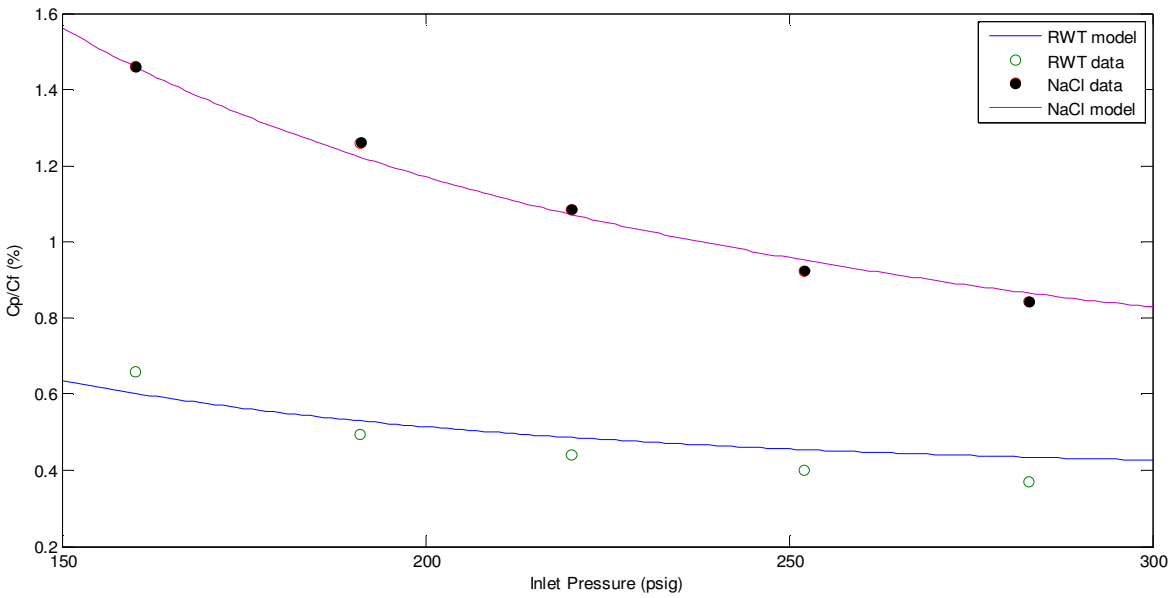


Figure 4.1: Rejection of NaCl and RWT at different pressures. C_p is the concentration of the solute in the permeate, and C_f is the concentration in the feed.

Figure 4.1 shows that rejection is higher when a higher pressure is applied on the feed side. However, higher pressure leads to more severe concentration polarization, which can lower or even reverse the improvement trend in rejection.

4.2 Characterization of Electrodialysis Stack

ED was characterized using NaCl, while recirculating the diluate, concentrate, and electrolyte streams. Conductivity was used to represent NaCl concentration, since it was the only salt present in the streams. Figure 4.2 shows the normalized change in conductivity vs. time for two different flow rates used and also comparing pulsed and continuous ED. Figure 4.2 shows that a higher flow rate allows more salt to be removed per time, and as expected, pulsing the voltage results in lower salt removal.

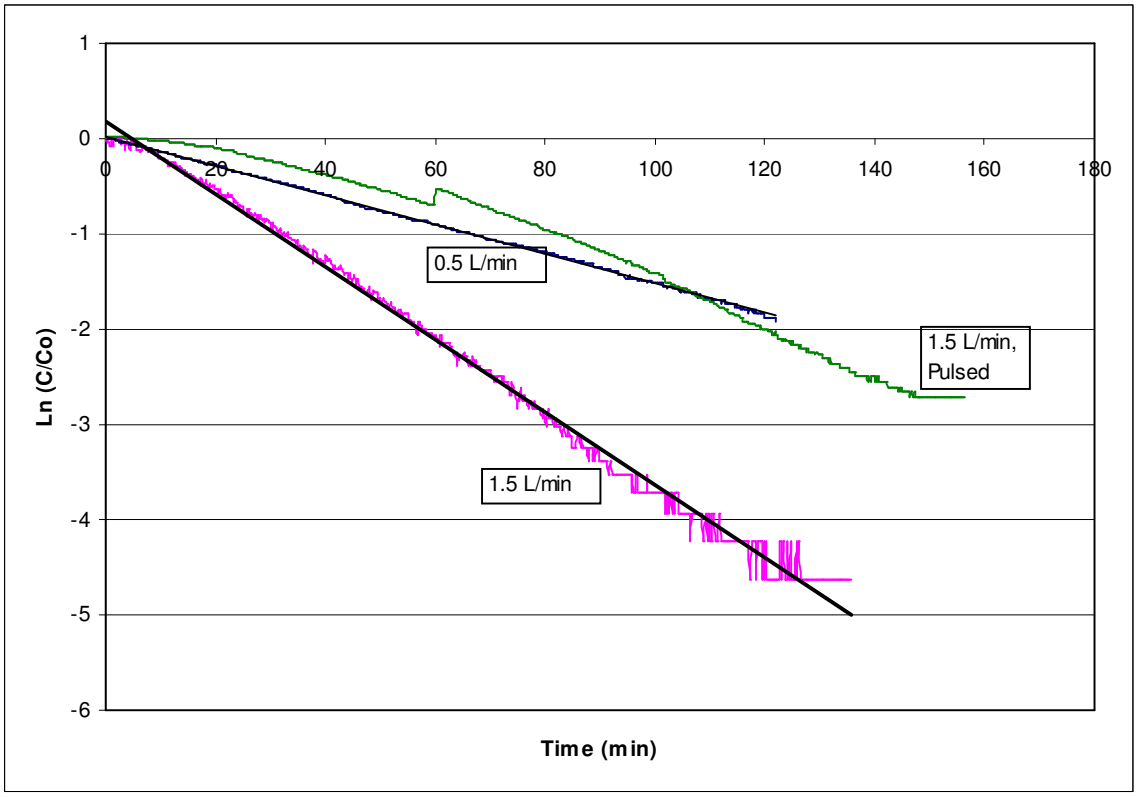


Figure 4.2: Normalized change in conductivity vs. time for an original concentration of 2 g/L NaCl and diluate and concentrate volumes of 20 L. The voltage applied was 20 VDC.

Figure 4.3 shows how the conductivity changes when taking into account the residence time. This shows that lower flow rates resulted in a higher fraction of salt being removed per pass, but because fewer passes through the ED stack occur with a lower flow rate, overall less salt is removed.

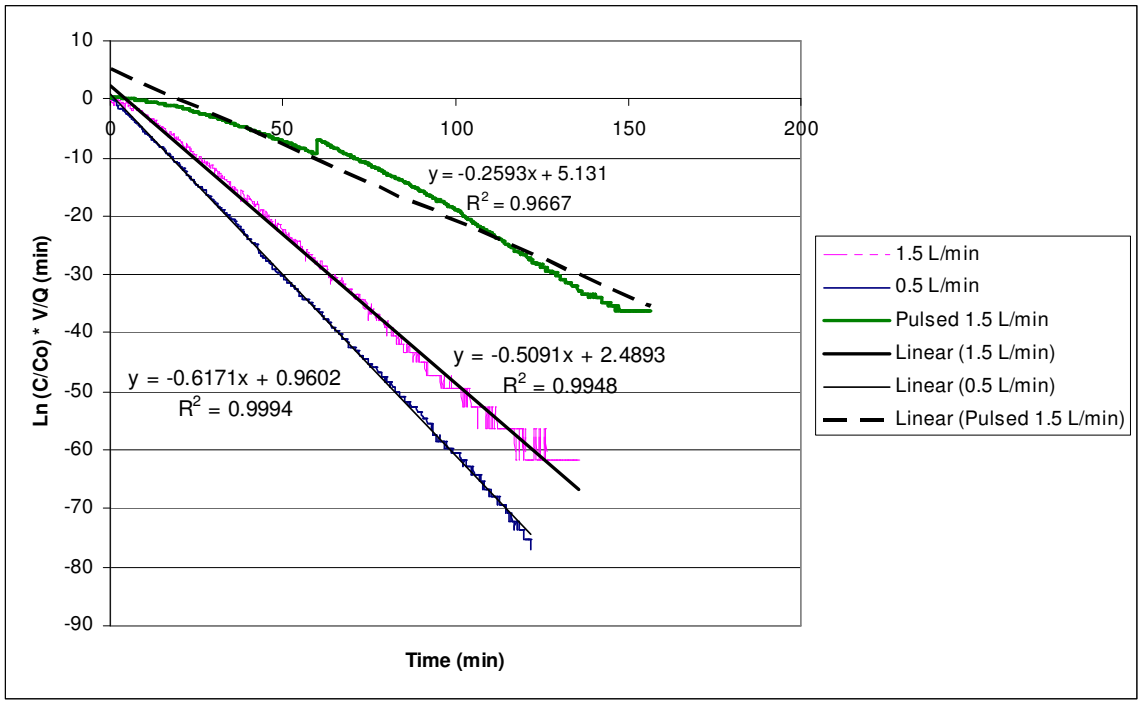


Figure 4.3: Change in normalized concentration of salt vs. time when taking residence time into account.

Using these data, ED can be modeled as removing a certain fraction of salt per pass through the stack. The equations below show how the mass balance can be modeled. Equation 4.1 is the original mass balance, while Equation 4.2 is the integrated form

$$V\frac{dC}{dt} = xCQ - CQ \qquad \text{Equation 4.1}$$

$$\ln\left(\frac{C}{C^0}\right) = \frac{(x-1)}{\tau}t \qquad \text{Equation 4.2}$$

Where V = diluate volume (L)

Q = diluate flow rate (L/min)

τ = residence time, or V/Q (min)

C^0 = initial concentration (g/L)

$-(x-1)$ = fraction of salt concentration removed per pass

C = the concentration at time t (g/L)

Equation 4.2 shows that there is a linear relationship between $\ln(C/C^0)$ and time, and this model agrees with Figures 4.2 and 4.3, which also show a linear relationship.

4.3 Tap Water Experiments

4.3.1 Preliminary RO/ED Experiments

Initial tap water experiments showed that combined RO and ED were effective at concentrating TOC. Table 4.1 shows that the TOC concentration factor is almost twice the water concentration factor, even though there is a buildup of TOC in the ED concentrate as well. However, in later experiments, this could not be reproduced. It is likely that organics were coming off the new ED membranes, misrepresenting the amount that was concentrated. Issues that occurred with RO were a rapid loss in flux, so that in subsequent experiments the tap water was filtered through a 10 µm and 1 µm cartridge filter and the feed pressure was lowered to mitigate concentration polarization and fouling. In all tables, Diluate refers to the water concentrated by RO, but having salts removed by ED (Figure 3.1). Concentrate refers to the ED concentrate, and Permeate the RO permeate.

Table 4.1: Results from Experiment 1 – combined RO/ED

Time (min)	Diluate TOC concentration (mg/L)	Concentrate TOC concentration (mg/L)	Permeate TOC concentration (mg/L)	Permeate volume* (L)	TOC concentration factor	Water concentration factor*
0	1.66			0	1.00	1.00
25	1.38	3.96	0.238	12	0.83	1.12
55	1.26	2.83	0.333	27	0.76	1.30
96	1.33	4.16	0.627	47	0.81	1.67
125	1.07	4.38	0.477	61	0.65	2.09
156	1.52	4.77	0.472	76	0.92	2.86
181	3.04	9.71	0.437	88	1.84	4.08
200	18.5	10	0.499	98	11.2	6.02

*Values are approximate

Pulsed and continuous ED were also compared in these preliminary experiments. As shown by Gurtler et al. (2008), pulsed ED was able to retain a greater fraction of TOC. These authors used a pulsing frequency of 0.25 Hz because it allowed enough time for qualitative observation of equilibration times. A frequency of 0.7 Hz was used here because it was the lowest frequency allowed by the pulse generator. Table 4.2 shows results from Experiments 2 through 4.

Experiment 3 (pulsed ED) had less TOC in the concentrate stream than Experiments 2 and 4 (continuous ED).

Table 4.2: TOC loss comparing continuous (Experiments 2 and 4) and pulsed (Experiment 3) ED

	Experiment 2	Experiment 3	Experiment 4
Final diluate TOC concentration (mg/L)	140	23.3	21.7
Final concentrate TOC concentration (mg/L)	30	4.06	6.92
TOC recovery	0.71	0.30	0.11

4.3.2 Isolating TOC Loss

In order to determine where TOC loss was coming from, the RO and ED processes were isolated. First, RO was used to concentrate the water about 9 times. As seen in Table 4.3, it was found that RO was able to retain most of the NOM, until about 4 times concentration, where a large loss in TOC was seen. It was postulated that this was due to calcium carbonate scaling and calcium bridging. In order to prevent calcium carbonate precipitation in the following experiments, HCl was added to keep the pH of the tap water around 7 during the RO process.

Table 4.3: TOC loss occurring during RO concentration with no pretreatment of tap water (Experiment 5)

% water remaining	TOC Concentration (mg/L)	TOC concentration factor (TOC/TOC_0)	Water concentration factor (V_0/V)	TOC recovery $[(TOC/TOC_0)/(V_0/V)]$
100.0	1.02	1.00	1.00	1.00
89.5	1.16	1.14	1.12	1.02
78.8	1.32	1.29	1.27	1.02
67.9	1.51	1.49	1.47	1.01
56.9	1.86	1.83	1.76	1.04
46.2	2.21	2.17	2.17	1.00
35.5	2.77	2.72	2.82	0.97
25.0	3.93	3.86	4.00	0.96
13.8	1.63	1.60	7.27	0.22
10.9	4.27	4.19	9.19	0.46

To isolate TOC change from running ED, water was first concentrated by 5 times with RO, and then run through ED only to examine TOC loss. In this experiment, both the concentrate and diluate streams were recirculated. Tables 4.4 and 4.5 show the results from both processes. RO is able to retain most of the NOM, as HCl had been added to keep the pH around 7. Table 4.5 shows that TOC loss does occur in ED, especially at higher applied voltage. Since the concentrate stream was recirculated, it is likely that ions and NOM are being removed more slowly (as salts accumulate in the concentrate stream) than if the concentrate stream were deionized water that only passed through the ED stack once, where there would be a larger driving force.

Table 4.4: RO concentration, adjusting pH to 7 (Experiment 7)

% water remaining	TOC Concentration (mg/L)	TOC concentration factor (TOC/TOC_0)	Water concentration factor (V_0/V)	TOC recovery [(TOC/TOC_0) / (V_0/V)
100.0	1.12	1.00	1.00	1.00
89.4	1.30	1.16	1.12	1.04
78.3	1.45	1.29	1.28	1.01
66.6	1.70	1.52	1.50	1.01
55.5	2.00	1.78	1.80	0.99
43.7	2.51	2.24	2.29	0.98
32.3	3.39	3.03	3.09	0.98
19.6	5.41	4.84	5.11	0.95

Table 4.5: TOC loss occurring through ED (Experiment 7)

Time (min)	Volts applied	TOC concentration (mg/L)	Conductivity (mS/cm)	% TOC retained [(TOC/TOC_0)/ (V_0/V)
0	20	5.41	1.75	0.95
30	20	5.26	1.66	0.92
60	20	4.92	1.64	0.86
90	40	4.11	1.3	0.72
120	40	3.15	0.85	0.55
150	40	2.41	0.5	0.42

As seen in Figure 2.4, if the membranes have a high selectivity for organics (see Section 4.4), unless the fraction of inorganic ions is much larger than the fraction of NOM, the anion

exchange sites will select NOM more preferentially, and some TOC will be lost by adsorption onto the membranes. Table 4.5 shows that the conductivity was relatively low, which indicates that the inorganic fraction is not high enough to prevent TOC loss, either by adsorption to the membrane or removal to the concentrate stream.

4.4 Ion Exchange Experiments

In an effort to retain the NOM in tap water, NaCl was added at 8.5 g/L to 20 L of concentrated tap water (expected to bring conductivity above 15 mS/cm, which was shown to be high enough to prevent TOC loss by Gurtler et al., 2008). Instead of TOC loss, the amount of TOC in the water increased, as chloride ions exchanged with NOM absorbed on the anion exchange membranes in previous runs. This verifies that a certain portion of TOC loss was due to absorption into the membranes, which agrees well with previous work that has found that adsorption of NOM on RO and ED membranes is diminished in the presence of NaCl (Lee and Elimelech, 2007; Kim et al., 2003; Koprivnjak et al., 2009; Gurtler et al. 2008). Figure 4.4 shows how the TOC concentration changes with time, at a constant conductivity of 18 mS/cm. After about 3 hours, the TOC concentration levels off. While running this experiment, the calcium concentration only decreased about half, from 86.6 mg/L to 45.3 mg/L.

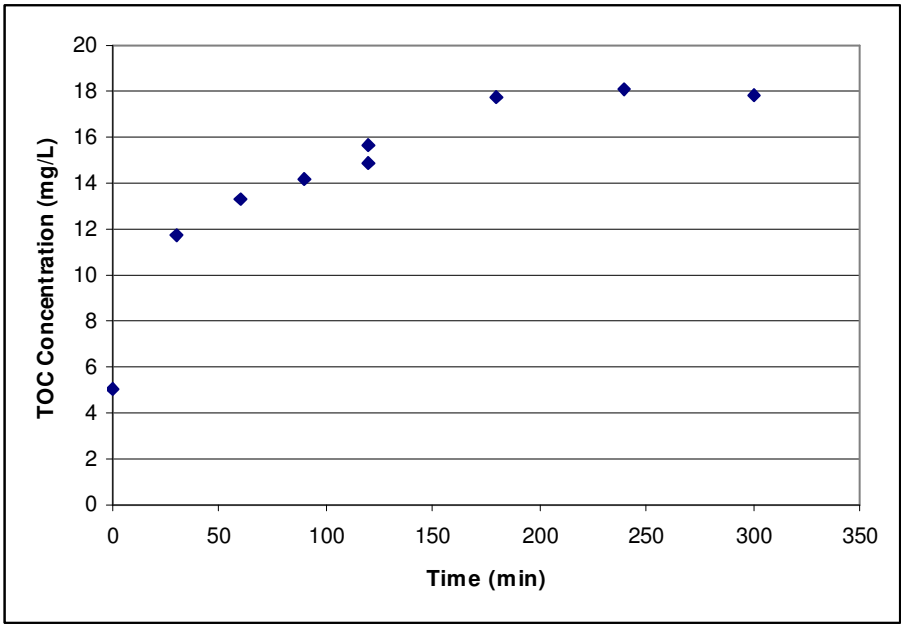


Figure 4.4: TOC changes with time while running ED with 5 times concentrated tap water with 8.5 g/L NaCl added (Experiment 8).

4.4.1 Salt Cleaning

Since the previous experiment showed that a relatively high concentration of NaCl could result in the release of NOM from the ion exchange membranes, cleaning with a high concentration of NaCl was attempted. Cleaning with high concentrations of NaCl resulted in TOC desorbing from the membranes. As seen in Figure 4.5, as more NaCl is added to both the diluate and concentrate streams, more chloride is able to exchange with TOC that is on the membranes, increasing the NOM concentration in solution.

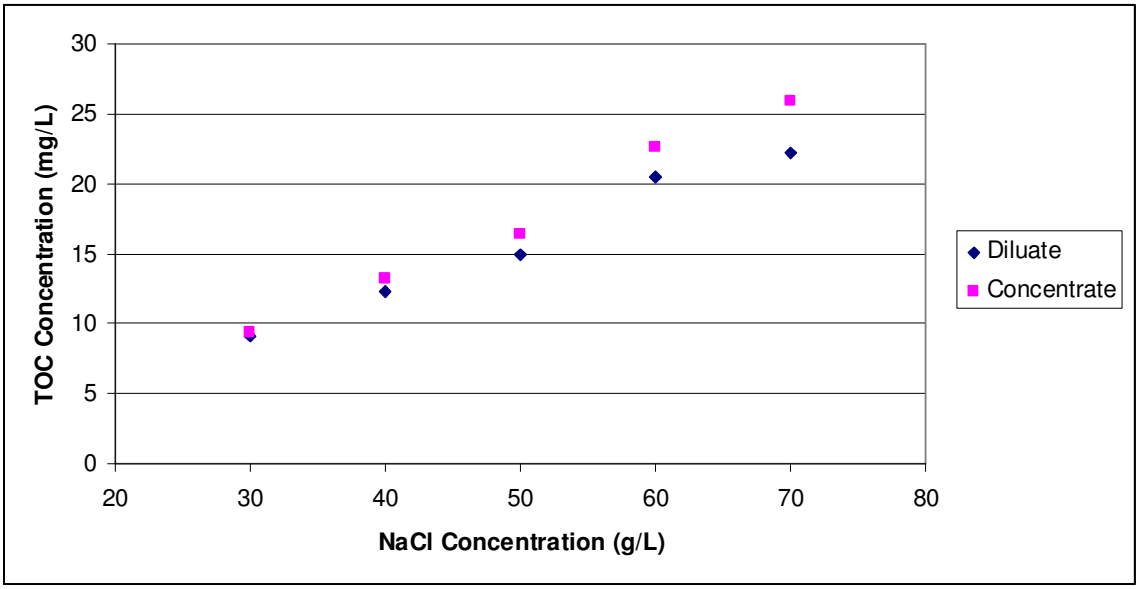


Figure 4.5: Increase in TOC concentration as increments of 10 g/L NaCl are added to both the diluate and concentrate streams.

A total of 8 batches of water were run through ED to clean the membranes, and 550.7 mg TOC was recovered. This was calculated by adding up the difference between initial and final TOC masses in each batch of water. NOM in Newmark tap water has a molecular weight in the range of approximately 80 g/mol to 3000 g/mol (Figure 4.6).

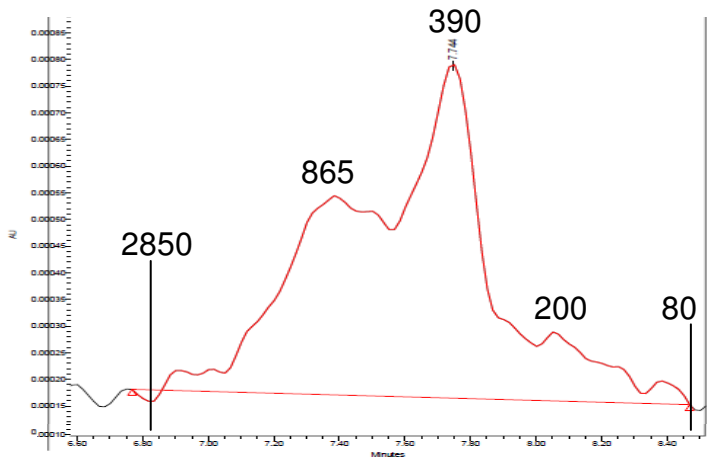


Figure 4.6: Size exclusion spectrum for Newmark tap water. The numbers indicate molecular weight in Daltons.

A molecular weight of 100 g/mol was chosen to represent this NOM, as it was assumed that the smaller NOM fraction was adsorbing to the membranes. This would mean that 5.5 meq was recovered from the membranes, which have a total capacity of 0.595 eq (see Section 4.5.1 for calculation). Thus, the amount of TOC removed in the cleaning experiment was about 0.9% of the total sites. If the NOM from all previous experiments (1.6 g total TOC for 10 experiments) had adsorbed onto the anion exchange membranes, only about 2.7% of the sites would be taken up by NOM. This shows the very high capacity for ED membranes to adsorb NOM.

4.4.2 Determining Sulfate vs. Chloride Selectivity

In order to examine sulfate/chloride selectivity, solutions of 4 g/L Na_2SO_4 were circulated through both the diluate and concentrate while the membranes were in chloride form. The selectivity constant, $K_{Cl}^{SO_4}$, for these membranes was calculated to be 0.09 from data obtained from the ion exchange experiments and Equations 4.3 to 4.5:

$$K_{Cl}^{SO_4} = \frac{[R_2SO_4][Cl^-]^2}{[RCl]^2[SO_4^{2-}]} \qquad \text{Equation 4.3}$$

$$[R_2SO_4] = \frac{V_{water}}{V_{membrane}}\left\{\left([SO_4^{2-}]_{initial} - [SO_4^{2-}]_{equilibrium}\right)_{dil} + \left(([SO_4^{2-}]_{initial} - [SO_4^{2-}]_{equilibrium}\right)_{conc}\right\}$$

Equation 4.4

$$[RCl] = Capacity - \frac{V_{water}}{V_{membrane}} \left\{ \left([Cl^-]_{equilibrium} - [Cl^-]_{initial} \right)_{dil} + \left([Cl^-]_{equilibrium} - [Cl^-]_{initial} \right)_{conc} \right\}$$

Equation 4.5

Where $[Cl^-]$ and $[SO_4^{2-}]$ are measured using ion chromatography.

This would yield an isotherm similar to Figure 2.3, which shows that sulfate is only preferred at concentrations less than 0.01 eq/L.

The selectivity constant for organics and chloride, K_{Cl}^{NOM}, is more difficult to estimate, due to the varying properties and sizes of NOM. Also, NOM must be concentrated from tap water, which also contains many other ions. Concentrated NOM that can be purchased is not representative of NOM in treated water (Malcom and MacCarthy, 1986), and so a synthetic solution cannot be made. However, from calculations using Equations 4.6 and 4.7 and data from the cleaning experiment, it is estimated to be between 0.75 and 20. Since it was not known how much NOM had adsorbed to the membrane from previous experiments, a value of 0.004 eq/L was chosen, assuming that nearly all of NOM had desorbed by the time an NaCl concentration of 70 g/L was used.

$$K_{Cl}^{NOM} = \frac{[RNOM][Cl^-]}{[RCl][NOM^-]}$$

Equation 4.6

$$[RNOM] = 0.004 - \frac{V_{water}}{V_{membrane}} \left\{ \left([NOM^-]_{equilibrium} - [NOM^-]_{initial} \right)_{dil} + \left([NOM^-]_{equilibrium} - [NOM^-]_{initial} \right) \right\}$$

Equation 4.7

The selectivity constant for organics and sulfate, $K_{SO_4}^{NOM}$, can be related to the previous two selectivity constants by the following equation:

$$K_{SO_4}^{NOM} = \frac{\left(K_{Cl}^{NOM} \right)^2}{K_{Cl}^{SO_4}}$$

Equation 4.8

With the values estimated here, $K_{SO_4}^{NOM}$ would be between 6.5 and 4600. Again this shows that in order for sulfate to be preferred over NOM, the total aqueous concentration must be low, or the fraction of sulfate in the aqueous phase must be very close to 1.

4.5 Tap Water with Salt Addition Experiments

In order to optimize TOC retention in ED, after concentrating tap water 5 times with RO, different concentrations of sulfate or chloride were added before and throughout running ED.

4.5.1 ED with Sulfate Addition

Figure 4.7 shows the change in TOC and chloride over time, with 0.5 g/L Na_2SO_4 addition, and Na_2SO_4 added throughout the experiment to keep the conductivity constant (~2.5 mS/cm).

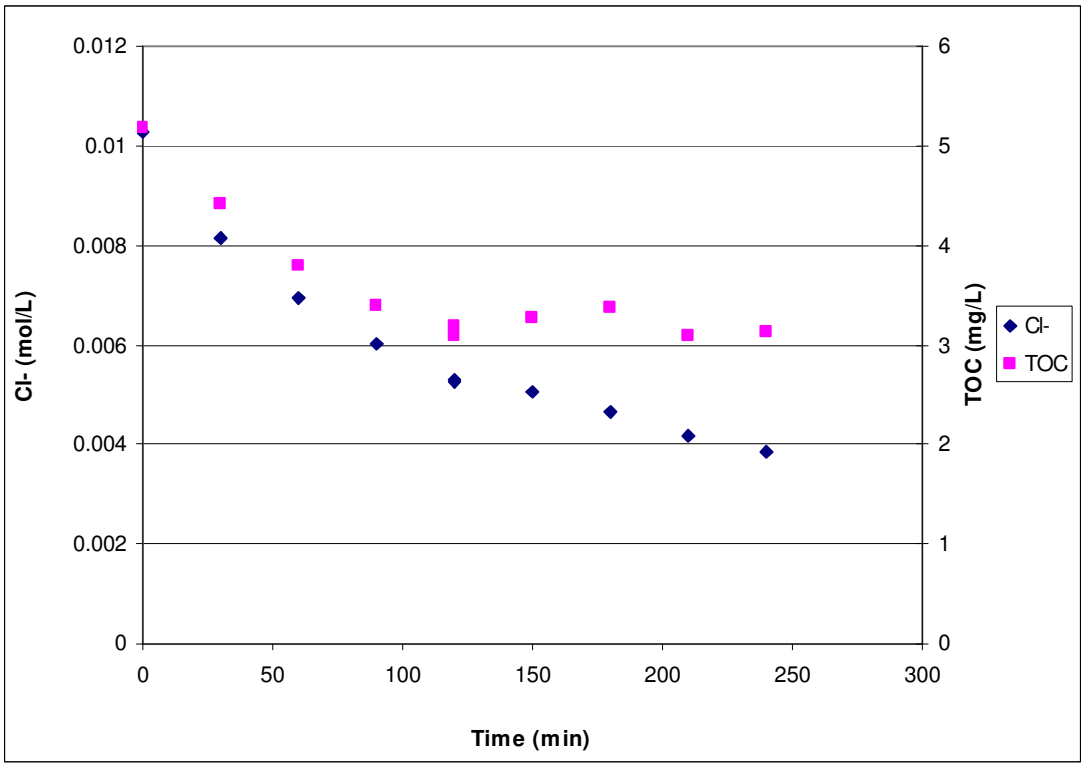


Figure 4.7: Change in TOC and chloride concentrations as the diluate stream is run through ED (Experiment 9). The anion exchange membranes were in sulfate form.

Figure 4.7 shows that the concentration change of chloride and TOC follow a similar trend, although TOC loss levels off within 2 hours, while the chloride concentration appears that it will levels off at a later time. Figure 4.8 compares the chloride removal with calcium removal. At this

concentration, calcium is removed faster than chloride. Although the ions are of different charges, the monovalent vs. divalent behavior agrees with ion exchange theory, where at lower concentrations, the divalent ion will be preferred on the ion exchange sites, and should be removed faster.

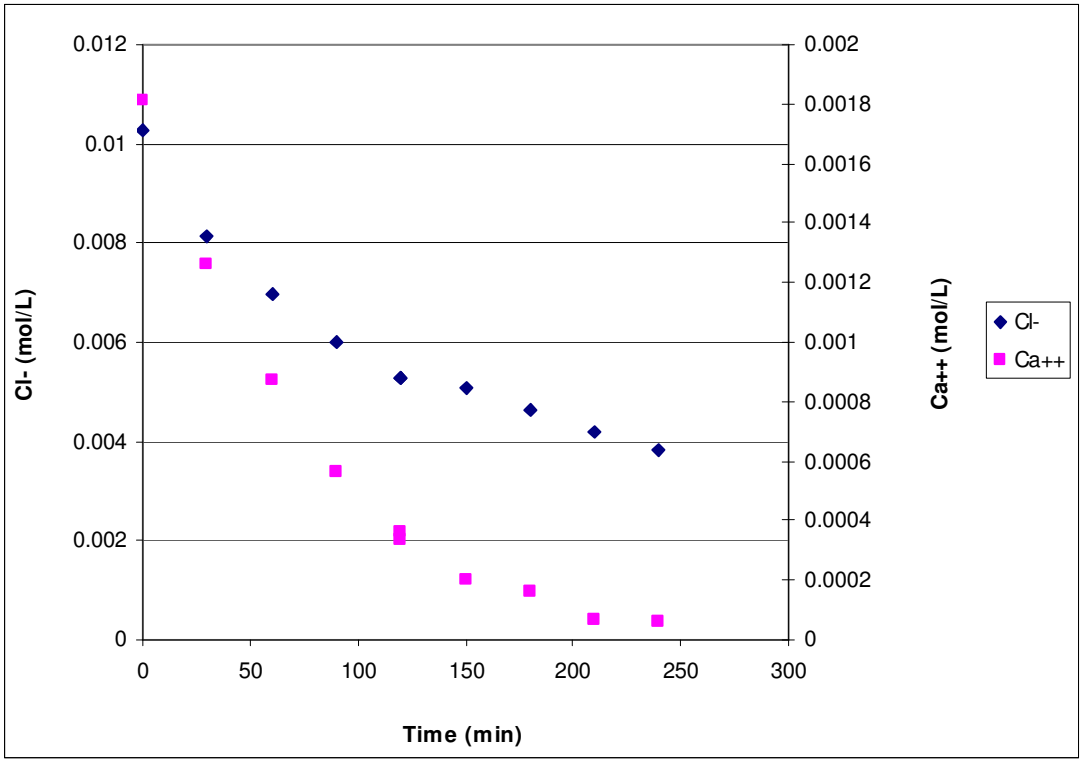


Figure 4.8: Change in calcium and chloride concentrations as the diluate stream is run through ED (Experiment 9). The anion exchange membranes were in sulfate form.

In order to see the effect of sulfate concentration, 1.7 g/L Na_2SO_4, which is just below the solubility limit for the amount of calcium in the water, was added before running the concentrated tap water through ED. Figure 4.9 shows how TOC and chloride concentrations change with time.

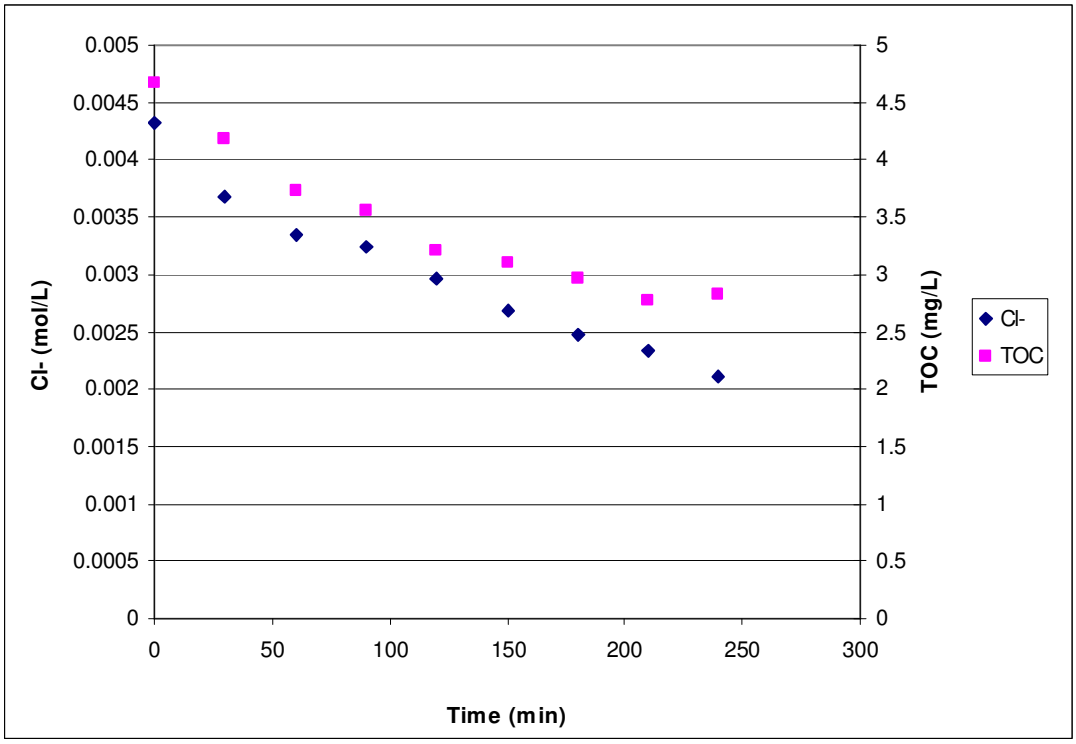


Figure 4.9: Change in TOC and chloride concentrations as the diluate stream is run through ED (Experiment 12). The anion exchange membranes were in sulfate form.

Once again, the chloride and TOC concentrations show a similar decrease at the beginning, but the TOC concentration levels off sooner. Although in Experiment 9 (0.5 g/L Na_2SO_4 addition), initial TOC loss was greater, after 4 hours, both Experiments 9 and 12 retained the same fraction of TOC (~60%).

A similar experiment was done, except with the anion exchange membranes in chloride form. The changes in chloride and TOC concentrations are seen in Figure 4.10.

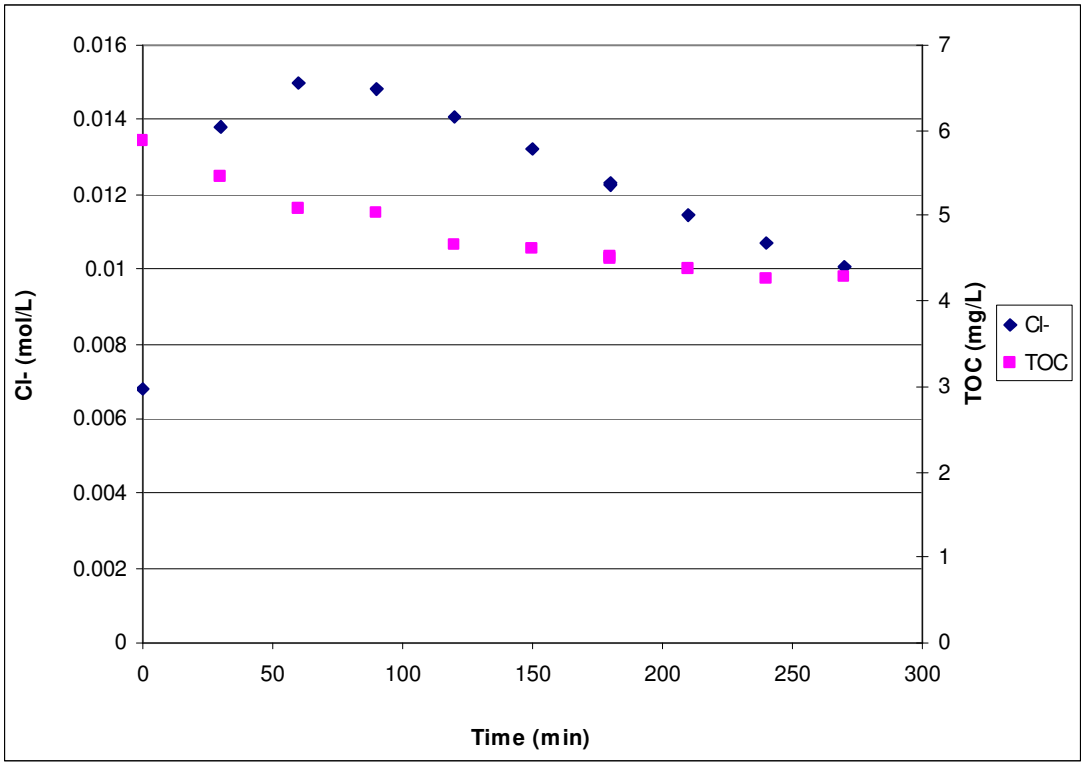


Figure 4.10: Change in TOC and chloride concentrations as the diluate stream is run through ED (Experiment 10). The anion exchange membranes were in chloride form.

Figure 4.10 shows an increase in chloride as chloride in the anion exchange membrane exchanges with sulfate in the aqueous solution. According to information from the manufacturer, GE, the capacity of the anion exchange membranes is 1.18 eq/L. The volume of the 30 anion exchange membranes is 0.504 L, which yields a total number of sites of 0.595 eq. From Figure 4.10, 0.184 eq Cl^- are displaced from the anion exchange membranes, whereas 0.565 eq SO_4^{2-} have been added to the tank. Therefore, not all of the chloride is displaced by sulfate, but the fraction of sulfate ions on the membranes increases as more sulfate is added as chloride is being removed. When the ED run was started with anion exchange membrane in chloride form, as much as 73% of TOC was retained in the diluate (Figure 4.10) as compared to 60% when the anion exchange membrane was in sulfate form (Figure 4.9).

4.5.2 ED with Chloride Addition

The previous experiment with sulfate addition successfully showed that an increase in sulfate concentration resulted in less TOC loss; however, it failed to distinguish the effect of sulfate vs.

chloride addition. In order to test that TOC loss was minimized due to sulfate addition and not just because of an increase in ion concentration, 1.6 g/L NaCl was added to concentrated water and run through ED in chloride form.

Figure 4.11 shows how calcium and sulfate concentrations change with time. Although they are both divalent, and the concentrations of Na^+ and Cl^- should be comparable, calcium shows a larger decrease over time, indicating that the cation exchange membrane selectivity for calcium over sodium is higher than the anion exchange membrane selectivity for sulfate over chloride.

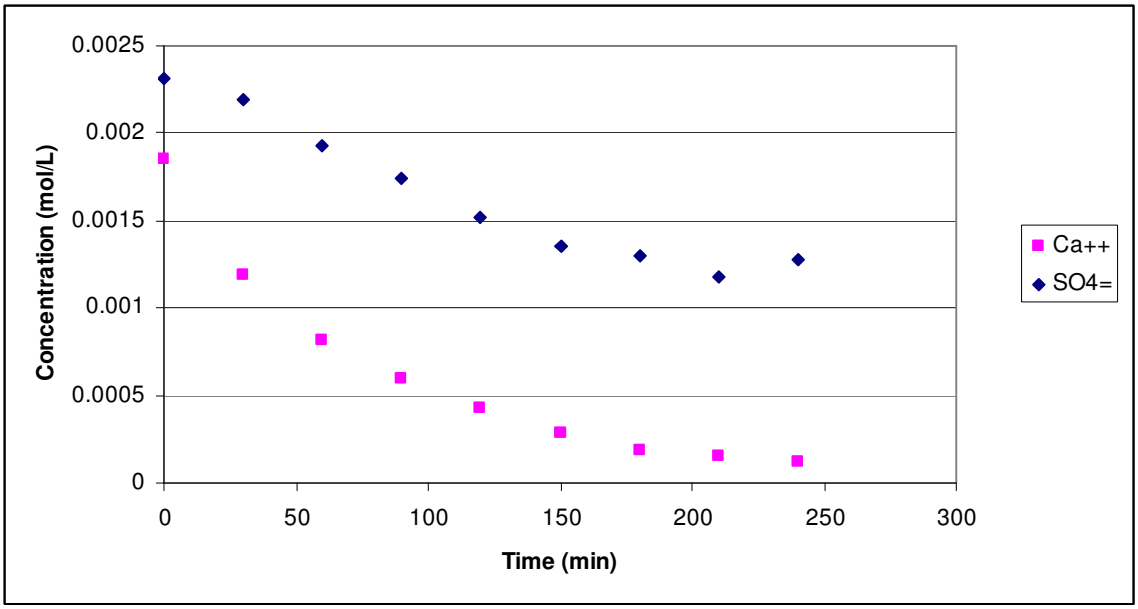


Figure 4.11: Change in calcium and sulfate concentrations as the diluate stream is run through ED (Experiment 13). The anion exchange membranes were in chloride form.

Figure 4.12 compares the change in TOC with the change in sulfate concentration. Sulfate is removed slightly slower than TOC. At this concentration, with x_{SO4} between 0.1 and 0.05, the monovalent ion will be preferred over the divalent ion in the membrane. More TOC was lost in Experiment 13 (chloride addition) than in the sulfate addition experiments. Only 44% of TOC was retained in the diluate when sodium chloride is added to the diluate stream (Figure 4.14, Experiment 13), whereas 60 – 73% of TOC was retained when sodium sulfate is added (Experiment 9, 10, 12). Interestingly, the conductivity level is higher (~6.5 mS/cm) during the

ED operation with sodium chloride addition (Experiment 13) than when sodium sulfate is added (3.93 mS/cm in Experiment 10). This indicates that conductivity is not the only parameter that controls NOM adsorption onto the anion exchange membrane, but valency of the anion is also important.

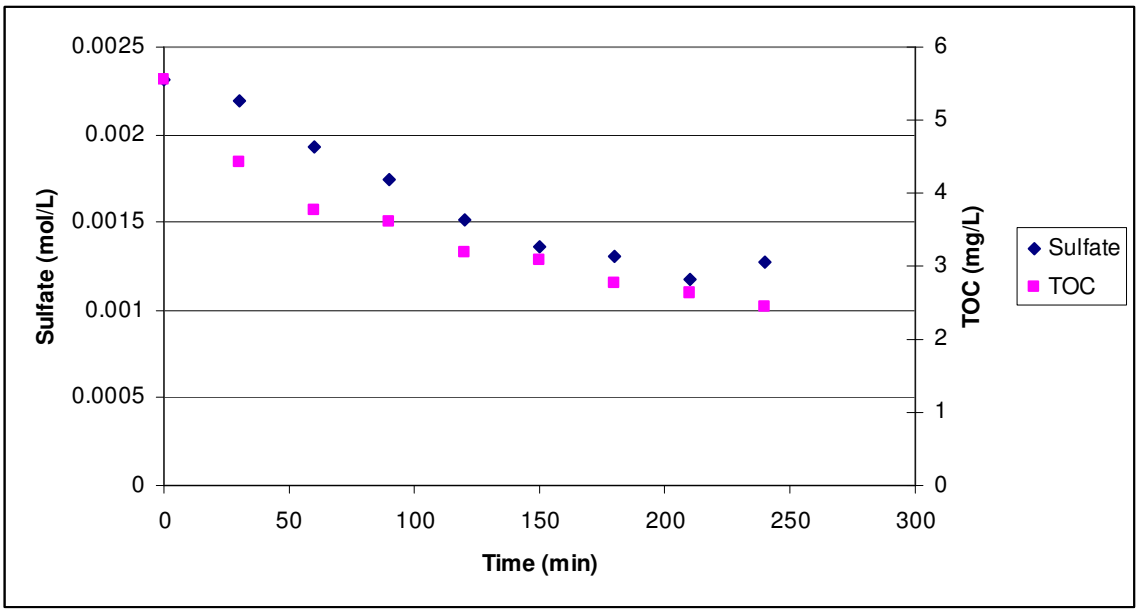
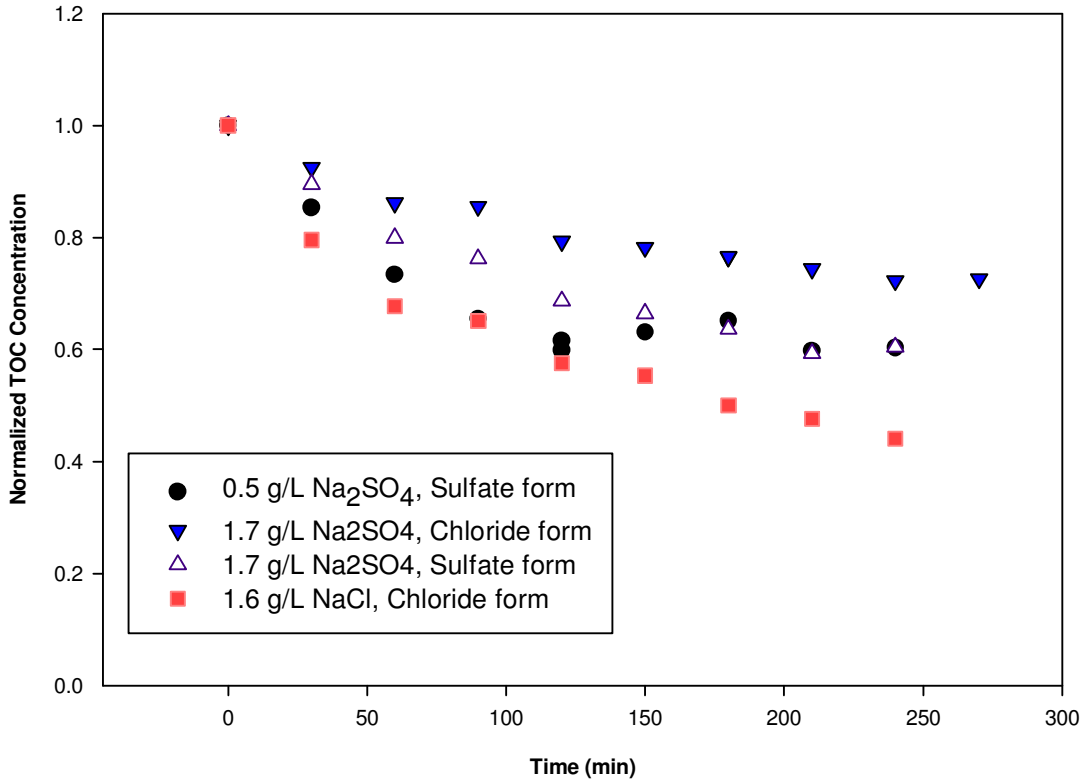


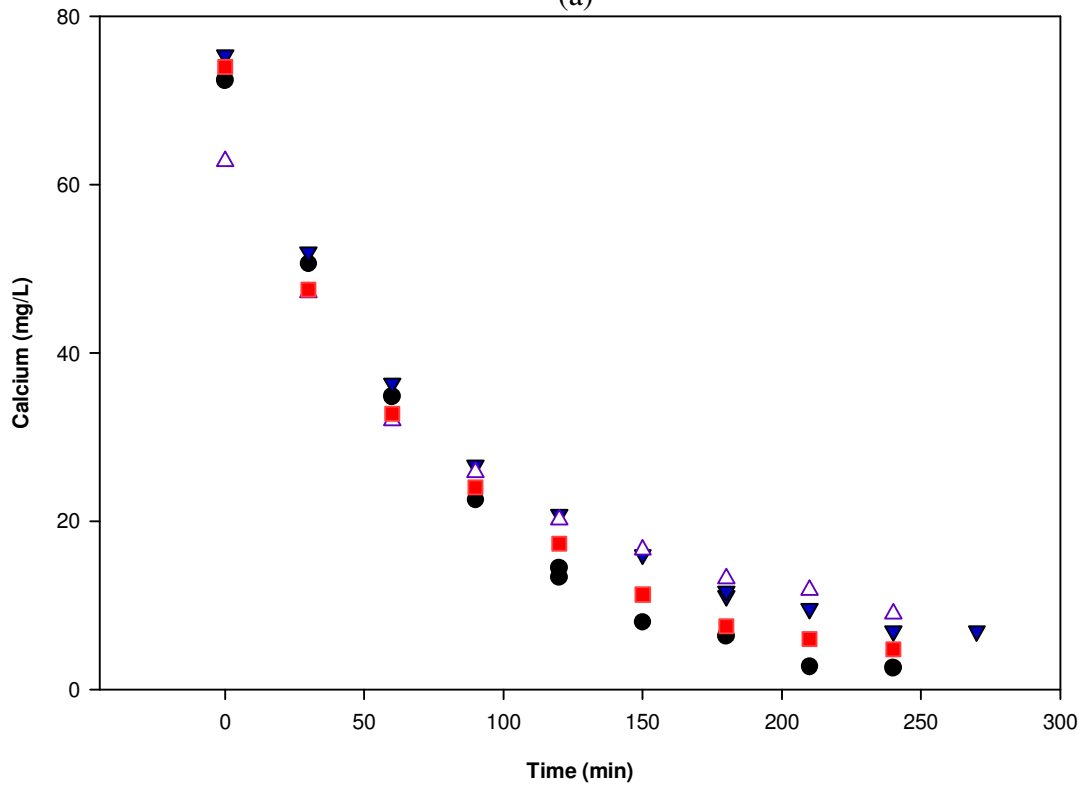
Figure 4.12: Change in TOC and sulfate concentrations as the diluate stream is run through ED (Experiment 13). The anion exchange membranes were in chloride form.

4.5.3 Comparison between Sulfate and Chloride Addition

Figure 4.13 shows the normalized concentrations of the previous experiments. Figure 4.13 shows that there is a trade-off between TOC retention and calcium removal. In order to retain TOC, either a high NaCl concentration or a high fraction of sulfate must be present in the diluate solution. However, a high NaCl concentration results in lower calcium removal (this was seen in the cleaning experiment where an NaCl concentration of 8.5 g/L was used), and the amount of sulfate needed to result in a high fraction in the aqueous phase cannot be added without precipitating calcium sulfate. Also, this high concentration of sodium sulfate will also result in lower calcium removal.



(a)



(b)

Figure 4.13: Changes in (a) TOC concentrations and (b) calcium concentrations after running ED with added amounts of solutes.

4.5.4 Final Concentration Experiment

Based on previous findings, adding a high concentration of NaCl (around 8 g/L) could retain NOM well while removing some calcium to allow the water to be concentrated further. In the final experiment, concentrating 224 L by 11.4 times with RO resulted in retaining 96% of TOC. By keeping the pH around 7, calcium carbonate precipitation was prevented. Subsequent ED operation with NaCl addition reduced the calcium concentration from 156 mg/L to 53 mg/L, but the TOC concentration also dropped from 11.7 mg/L to 8.9 mg/L, resulting in 73% retention of TOC. Upon adding 98 L and concentrating down to 15 L, again the RO was able to retain TOC, at 76% of what should originally be in the total 322 L. ED was run again, this time with no salt addition, and the calcium concentration was reduced from 132 mg/L to 76 mg/L, while TOC decreased from 17.6 mg/L to 14.0 mg/L. The result was 60% retention of TOC.

Although 8 g/L NaCl resulted in less TOC loss than lower concentrations of sulfate or chloride, it resulted in much lower calcium removal. Lower concentrations of sodium would be necessary to remove more calcium, but without being able to replace chloride with sulfate, TOC loss would continue to occur.

CHAPTER 5: CONCLUSIONS

5.1 Summary of Results and Recommendations

TOC loss was mainly attributed to TOC adsorption to the ion exchange membranes as well as TOC passing through the membranes into the ED concentrate. TOC loss from ED can be minimized by adding NaCl or Na_2SO_4 to the diluate stream. Sulfate addition is more effective than chloride for retaining NOM when the sulfate fraction in the aqueous phase is high or the total ion concentration is low. A high concentration of sodium chloride displaces NOM that adsorbs to anion exchange sites on the membranes, and is able to prevent loss of NOM. However, calcium is removed slowly due to the high sodium concentration, which limits the amount of sulfate that can be added when trying to bring the conductivity lower. Adding sulfate in low concentrations (low enough to prevent calcium sulfate precipitation) results in an initial loss of NOM, but eventually no further loss occurs as sulfate takes over the anion exchange sites. However, it is unable to remove all the calcium, and limits further concentration due to the risk of calcium sulfate precipitation.

In order to optimize NOM concentration with RO, the tap water should first be filtered with 1 micron or 0.3 micron filters (in future experiments) to remove colloids that could clog the membrane. The pump should be run at around half the recommended feed pressure in order to reduce the effects of concentration polarization and fouling. Also, when high calcium concentrations and alkalinity are present in the water, the pH should be adjusted to 7 to prevent calcium carbonate scaling. In order to prevent the membrane from being exposed to pressurized air, the water should not be concentrated to low volumes (less than 10 L).

To allow ED to remove many of the inorganic ions while retaining NOM, sulfate should be added while running ED to flush out the other ions. Once those ions have been removed, sulfate can be removed to result in water with a high concentration of NOM but low salt content. In order for this to be possible for the tap water used in this study, pretreatment must occur to remove the calcium ions.

5.2 Future Work

In order to remove the limitation of the amount of sulfate that can be added, and to avoid precipitation problems, calcium removal using an inorganic zeolite will be implemented before RO concentration. This should result in better TOC retention, as a higher concentration of sulfate can be added and will be able to flush out other inorganic anions, while being preferred over NOM in the anion exchange membranes. The presence of silica should also be monitored to ensure that silica precipitation will not occur.

Other conditions to optimize are the pulsing frequency as well as the number of cell pairs in the ED stack. Once an appropriate concentration scheme is determined using Newmark tap water, treated water from Bloomington (before chlorination) will be used for the DBP studies.

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APPENDIX A– Summary of Experimental Methods

Date of experiment	Experiment/ Appendix	RO conditions	ED conditions	Protocol
10/7/11	1 B	Qf = 9.56 Lpm Pin = 247 psi Pout = 240 psi	Q = 1-1.5 Lpm Continuous	Run RO and ED simultaneously the whole experiment
10/31/11	2 B	Qf = 9.5-9.7 Lpm Pin = 253 psi Pout = 247 psi	Q = 1-1.5 Lpm Continuous	Run RO for whole experiment; introduce ED when conductivity is around 2 mS/cm
11/20/11	3 B	Qf = 9.14 Lpm Pin = 147 psi Pout = 144 psi	Q = 1-1.5 Lpm Pulsed	Run RO for whole experiment; introduce ED when conductivity is around 2 mS/cm; pressure lowered to reduce fouling
12/1/11	4 B	Qf = 9.5 Lpm Pin = 250 psi Pout = 244 psi	Q = 1-1.5 Lpm Continuous	Run RO for whole experiment; introduce ED when conductivity is around 2 mS/cm; higher pressure applied due to severe fouling
12/12/11	5 B	Qf = 8.28 Lpm Pin = 123 psi Pout = 119 psi		Run RO only
12/20/11	6 B	Qf = 9.24 Lpm Pin = 149 psi Pout = 144 psi	Q = 1-1.5 Lpm Continuous	Run RO for whole experiment, keeping pH around 7; introduce ED when conductivity is around 1 mS/cm
12/22/11	7 B	Qf = 8.8 Lpm Pin = 154 psi Pout = 148 psi	Q = 1-1.5 Lpm Pulsed	Run RO to concentrate 5 times, keeping pH around 7; stop RO and introduce ED
1/12/12	8 D	Qf = 9.6 Lpm Pin = 156 psi Pout = 152 psi	Q = 0.85 Lpm Continuous One pass concentrate (from now on)	Run RO to concentrate 5 times, keeping pH around 7; add 8.5 g/L (168 g) NaCl and run ED; keep adding NaCl to keep conductivity high
2/27/12	9 D	Qf = 9.1 Lpm Pin = 156 psi Pout = 153 psi	Q = 0.85 Lpm Pulsed Sulfate form	Run RO to concentrate 5 times, keeping pH around 7; add 0.5 g/L (12 g) Na_2SO_4; keep adding Na_2SO_4 to keep conduct-

				ivity around 2.5 mS/cm
3/14/12	10 D	Qf = 9.1 Lpm Pin = 159 psi Pout = 154 psi	Q = 0.85 Lpm Pulsed Chloride form	Run RO to concentrate 5 times, keeping pH around 7; add 1.7 g/L (40.1 g) Na_2SO_4; keep adding Na_2SO_4 to keep conductivity around 3.9 mS/cm (total 18.92 g Na_2SO_4 added in 4.5 hours)
3/19/12	11 D	Qf = 9.1 Lpm Pin = 159 psi Pout = 155 psi	Q = 0.85 Lpm Pulsed Chloride form	Add 1.8 g/L (212 g) Na_2SO_4; run RO and ED simultaneously with no further salt addition
3/21/12	12 D	Qf = 9.1 Lpm Pin = 158 psi Pout = 154 psi	Q = 0.85 Lpm Pulsed Sulfate form	Run RO to concentrate 5 times, keeping pH around 7; add 1.7 g/L (40.3 g) Na_2SO_4; keep adding Na_2SO_4 to keep conductivity around 3.9 mS/cm (total 10.87 g Na_2SO_4 added in 4 hours)
3/23/12	13 D	Qf = 9.1 Lpm Pin = 160 psi Pout = 155 psi	Q = 0.85 Lpm Pulsed Chloride form	Run RO to concentrate 5 times, keeping pH around 7; add 1.6 g/L (32.9 g) NaCl; keep adding NaCl to keep conductivity around 6.5 mS/cm (total 31 g NaCl added in 4 hours)
3/30/12-4/6/12	14 D	Qf = 9.2 Lpm Pin = 164 psi Pout = 160 psi	Q = 0.85 Lpm Pulsed Chloride form	Run RO to concentrate until just below calcium sulfate solubility limit. Add 8.1 g/L (160 g) NaCl, run ED. Refill tank, concentrate a total of around 21.5 times. Run ED.

APPENDIX B – Tap Water Experiments

1

Date 10/7/11
Protocol: Run RO and ED simultaneously the whole experiment. Conductivity was kept around 0.3 mS/cm.

Time (min)	Diluate TOC concentration (mg/L)	Concentrate TOC concentration (mg/L)	Permeate TOC concentration (mg/L)	Permeate volume* (L)	TOC concentration factor	Water concentration factor*
0	1.657			0	1.00	1.00
25	1.377	3.959	0.2384	12	0.83	1.12
55	1.262	2.827	0.3335	27	0.76	1.30
96	1.334	4.165	0.6269	47	0.81	1.67
125	1.075	4.385	0.4769	61	0.65	2.09
156	1.519	4.766	0.4715	76	0.92	2.86
181	3.041	9.705	0.4367	88	1.84	4.08
200	18.49	10	0.499	98	11.16	6.02

*Values are approximate

2

Date 10/31/11

Protocol: RO concentration. Introduce ED when conductivity is around 2 mS/cm, and run ED to keep conductivity at this value. ED is continuous (not pulsed).

Actual time	Time (min)	Diluate* TOC (mg/L)	Concen-trate TOC (mg/L)	Perm-eate TOC (mg/L)	Perm-eate volume (L)	% water remain-ing	Volume remain-ing (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remain-ing
1:00	0	2.937			0	100.0	118	1.00	1.00	1.00
2:00	60	1.84		0.312	24.546	79.2	93.454	0.63	1.26	0.50
2:30	90	3.2		0.26	36.726	68.9	81.274	1.09	1.45	0.75
3:00	120	2.81		0	48.636	58.8	69.364	0.96	1.70	0.56
3:30	150	3.1		0.12	60.316	48.9	57.684	1.06	2.05	0.52
4:00	180	4.4		0.74	71.866	39.1	46.134	1.50	2.56	0.59
4:30	210	5.4		0.26	83.696	29.1	34.304	1.84	3.44	0.53
5:00	240	8.9		0.18	95.496	19.1	22.504	3.03	5.24	0.58
5:30	270	17.7	0.43	0.61	106.646	9.6	11.354	6.03	10.39	0.58
6:00	300	52.1	24.3	0.88	111.816	5.2	6.184	17.74	19.08	0.93
Final	330	140.1	30		116.236	1.5	1.764	47.70	66.89	0.71

*RO reject/ED diluate

3

Date 11/20/11

Protocol: RO concentration. Introduce ED when conductivity is around 2 mS/cm, and run ED to keep conductivity at this value. ED is pulsed. RO was run with decreased feed pressure to reduce fouling.

Actual time	Time (min)	Diluate TOC (mg/L)	Concen-trate TOC (mg/L)	Perm-eate TOC (mg/L)	Perm-eate volume (L)	% water remain-ing	Volume remain-ing (L)	TOC concen-tration factor	Water concen-tration factor	Frac-tion of TOC remain-ing
10:14	0	1.062			0	100.0	118.52	1.00	1.00	1.00
11:44	90	1.454		0.222	16.17	86.4	102.35	1.37	1.16	1.18
13:04	170	1.424		0.1996	29.995	74.7	88.525	1.34	1.34	1.00
14:14	240	2.05		0.1704	42.175	64.4	76.345	1.93	1.55	1.24
15:24	310	2.108		0.2569	54.456	54.1	64.064	1.98	1.85	1.07
16:34	380	2.714		0.2742	66.561	43.8	51.959	2.56	2.28	1.12
17:44	450	2.963		0.2315	78.201	34.0	40.319	2.79	2.94	0.95
18:54	520	4.054		0.3359	89.381	24.6	29.139	3.82	4.07	0.94
20:24	610	6.455		0.3314	101.876	14.0	16.644	6.08	7.12	0.85
21:30	670	9.296		0.3059	107.246	9.5	11.274	8.75	10.51	0.83
22:55	760	10.91	0.8549	0.4531	113.856	3.9	4.664	10.27	25.41	0.40
Final		23.26	4.059		116.916	1.4	1.604	21.90	73.89	0.30

4

Date 12/01/11

Protocol: RO concentration. Introduce ED when conductivity is around 2 mS/cm, and run ED to keep conductivity at this value. ED is continuous (not pulsed).

Actual time	Time (min)	Diluate TOC (mg/L)	Concen-trate TOC (mg/L)	Perm-eate TOC (mg/L)	Perm-eate volume (L)	% water remain-ing	Volume remain-ing (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remain-ing
10:04	0	1.043			0	100.0	119.19	1.00	1.00	1.00
11:00	60	1.282		0.1111	11.33	90.5	107.86	1.23	1.11	1.11
12:00	120	1.253		0.1248	22	81.5	97.19	1.20	1.23	0.98
13:00	180	1.383		0.09754	32.66	72.6	86.53	1.33	1.38	0.96
14:13	253	1.708		0.1146	45.32	62.0	73.87	1.64	1.61	1.01
15:23	323	1.817		0.07924	57.79	51.5	61.4	1.74	1.94	0.90
16:33	393	2.278		0.106	70.34	41.0	48.85	2.18	2.44	0.90
17:53	473	2.956		0.0865	83.06	30.3	36.13	2.83	3.30	0.86
19:23	563	4.43		0.1471	95.62	19.8	23.57	4.25	5.06	0.84
21:13	673	7.826		0.2524	106.52	10.6	12.67	7.50	9.41	0.80
23:20	800	13.41	4.841	0.513	112.53	5.6	6.66	12.86	17.90	0.72
2:20	1160	21.73	6.916		118.54	0.5	0.65	20.83	183.37	0.11

Notes: Fouling caused extremely low flux

5

Date 12/12/11
Protocol: Concentrate about 9 times with RO.

Actual time	Diluate TOC (mg/L)	pH	Permeate TOC (mg/L)	Permeate volume (L)	% water remaining	Volume remaining (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining
3:25	1.018			0	100.0	119.89	1.00	1.00	1.00
4:17	1.164	8.64	0.2481	12.58	89.5	107.31	1.14	1.12	1.02
5:07	1.318	8.63	0.2054	25.44	78.8	94.45	1.29	1.27	1.02
5:57	1.514	8.69	0.1789	38.52	67.9	81.37	1.49	1.47	1.01
10:30	1.86	8.71	0.1365	51.675	56.9	68.215	1.83	1.76	1.04
11:21	2.205	8.76	0.1635	64.525	46.2	55.365	2.17	2.17	1.00
12:12	2.771	8.84	0.1685	77.355	35.5	42.535	2.72	2.82	0.97
1:03	3.927	8.84	0.1724	89.905	25.0	29.985	3.86	4.00	0.96
1:57	1.625	8.84	0.1706	103.4	13.8	16.49	1.60	7.27	0.22
2:12	4.265	8.87		106.85	10.9	13.04	4.19	9.19	0.46

6

Date 12/20/11

Protocol: RO concentration, maintaining a pH of 7. Introduce ED when conductivity is around 1 mS/cm, and run ED to keep conductivity at this value.

Actual time	Diluate TOC (mg/L)	Concen-trate TOC (mg/L)	Perm-eate TOC (mg/L)	Perm-eate volume (L)	% water remain-ing	Volume remain-ing (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remain-ing
2:47	1.291			0	100.0	119.24	1.00	1.00	1.00
3:25	1.376		0.3364	12.55	89.5	106.69	1.07	1.12	0.95
4:05	1.585		0.3424	26.72	77.6	92.52	1.23	1.29	0.95
4:45	1.835		0.2943	40.205	66.3	79.035	1.42	1.51	0.94
5:20	2.087		0.301	52.455	56.0	66.785	1.62	1.79	0.91
6:00	2.626		0.2643	65.805	44.8	53.435	2.03	2.23	0.91
10:15	3.439		0.2961	79.155	33.6	40.085	2.66	2.97	0.90
10:55	5.525		0.2981	92.325	22.6	26.915	4.28	4.43	0.97
11:35	7.164	6.68	0.2982	105.02	11.9	14.22	5.55	8.39	0.66
12:13	14.73	8.367		116.53	2.3	2.71	11.41	44.00	0.26

7

Date 12/22/11
Protocol: RO concentration, maintaining a pH of 7. Run ED. Concentrate stream was recirculated.

RO concentration:

Actual time	TOC concen-tration (mg/L)	Permeate TOC concen-tration (mg/L)	Permeate volume (L)	% water remaining	Volume remaining (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining
9:23	1.119		0	100.0	117.84	1.00	1.00	1.00
10:03	1.297	0.09266	12.49	89.4	105.35	1.16	1.12	1.04
10:43	1.448	0.08128	25.545	78.3	92.295	1.29	1.28	1.01
11:23	1.698	0.08554	39.3	66.6	78.54	1.52	1.50	1.01
12:03	1.996	0.1009	52.445	55.5	65.395	1.78	1.80	0.99
12:43	2.511	0.09252	66.385	43.7	51.455	2.24	2.29	0.98
1:23	3.392	0.08806	79.76	32.3	38.08	3.03	3.09	0.98
2:06	5.414	0.09784	94.76	19.6	23.08	4.84	5.11	0.95

ED:

Time (min)	Volts applied	TOC concentration (mg/L)	Conductivity (mS/cm)	TOC concentration factor	Water concentration factor	Fraction of TOC remaining	Fraction of TOC not removed by ED
0	20	5.414	1.75	4.84	5.11	0.95	1.00
30	20	5.257	1.66	4.70	5.11	0.92	0.97
60	20	4.918	1.64	4.39	5.11	0.86	0.91
90	40	4.112	1.3	3.67	5.11	0.72	0.76
120	40	3.153	0.85	2.82	5.11	0.55	0.58
150	40	2.414	0.5	2.16	5.11	0.42	0.45

APPENDIX C – Ion Exchange Experiments

Salt Cleaning Experiment

Protocol: In both diluate and concentrate streams: 30g/L, 40g/L, 50g/L, 60g/L, 70g/L NaCl (same 4 L batch of water, 2 hours between additions)

NaCl (g/L)	Diluate TOC (mg/L)	Concentrate TOC (mg/L)	Diluate Ca++ (mg/L)	Concentrate Ca++ (mg/L)	Diluate SO4= (mol/L)	Concentrate SO4= (mol/L)
30	9.184	9.373	61.0	57.1	0.004121	0.003648
40	12.32	13.2	81.4	80.5	0.004812	0.004232
50	14.96	16.41	99.1	86.8	0.005318	0.005129
60	20.51	22.65	122.5	108.2	0.006711	-
70	22.22	25.92	139.4	122.5	0.006956	0.006699

Determining Sulfate vs. Chloride Selectivity

Protocol: Add 4 g/L Na_2SO_4 to both 6 L of diluate and concentrate streams. After 2 hours, add 6 g Na_2SO_4 to each tank.

	Na2SO4 (mg/L)	NaCl (mg/L)	SO4= (mol/L)	Cl- (mol/L)
Diluate initial (4 g/L Na2SO4)	3440	56	0.0242	0.0010
Concentrate initial (4 g/L Na2SO4)	4320	41	0.0304	0.0007
Diluate after 2 hours	2180	1817	0.0154	0.0311
Concentrate after 2 hours	2127	1815	0.0150	0.0311
Diluate for 2 hours after adding 1 g/L Na2SO4	3121	1961	0.0220	0.0336
Concentrate for 2 hours after adding 1 g/L Na2SO4	3058	1943	0.0215	0.0333

APPENDIX D – Tap Water with Salt Addition Experiments

8

Date 1/12/12
Protocol: RO concentration, maintaining a pH of 7. Add 168 g NaCl (8.5 g/L), run ED with subsequent NaCl addition. ED was in mixed form.

RO concentration:

Actual time	TOC concen-tration (mg/L)	Permeate TOC concen-tration (mg/L)	Permeate volume (L)	% water remaining	Volume remaining (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining
10:20	0.8788		0	100.0	117.66	1.00	1.00	1.00
10:58	1.0150	0.1735	13.03	88.9	104.63	1.15	1.12	1.03
11:34	1.1896	0.1930	26.22	77.7	91.44	1.35	1.29	1.05
12:12	1.3652	0.1765	39.48	66.4	78.18	1.55	1.50	1.03
12:51	1.6211	0.1329	53.39	54.6	64.27	1.84	1.83	1.01
1:41	2.3016	0.1267	70.97	39.7	46.69	2.62	2.52	1.04
2:19	3.1259	0.1014	84.85	27.9	32.81	3.56	3.59	0.99
2:56	5.0950	0.0973	97.83	16.9	19.83	5.80	5.93	0.98

ED:

Time (min)	Volts applied	TOC concentration (mg/L)	Conductivity (mS/cm)	Ca++ (mg/L)	Ca++ (mol/L)
0	20	5.05	18.77	86.6	0.00216
30	20	11.77	18.25	88.8	0.00222
60	20	13.30	17.99	92.8	0.00232
90	20	14.15	17.9	80.8	0.00202
120	20	14.83	18.1	76.6	0.00191
120	20	15.67	18.5	76.4	0.00191
180	20	17.77	17.35	69.1	0.00173
240	20	18.11	17.5	61.7	0.00154
300	20	17.81	16.3	53.2	0.00133
360	20	17.06	15.1	44.0	0.00110
420	20	16.53	15.27	37.7	0.00094
420	20	15.43	18.4	49.0	0.00123
450	20	16.86	17.9	38.8	0.00097
495	20	17.58	17.7	43.2	0.00108
540	20	17.92	18	40.8	0.00102
600	20	18.53	18.1	41.3	0.00103
600	15	18.43	18.43	44.0	0.00110
660	15	19.47	19.47	47.9	0.00120
720	15	19.35	19.35	47.6	0.00119
780	15	19.87	19.87	45.3	0.00113

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Date 2/27/12

Protocol: RO concentration, maintaining a pH of 7. Add 12.0 g Na_2SO_4 (0.5 g/L), run ED with subsequent Na_2SO_4 addition. ED originally in sulfate form.

RO concentration:

Actual time	TOC concen-tration (mg/L)	Permeate TOC concen-tration (mg/L)	Permeate volume (L)	% water remaining	Volume remaining (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining
10:00	1.3125		0	100.0	117.87	1.00	1.00	1.00
10:32	1.4745	0.2466	13.145	88.8	104.725	1.12	1.13	1.00
11:15	1.6475	0.2169	27.095	77.0	90.775	1.26	1.30	0.97
11:50	1.8815	0.2182	40.275	65.8	77.595	1.43	1.52	0.94
12:30	2.1895	0.2614	53.51	54.6	64.36	1.67	1.83	0.91
1:10	2.6945	0.2597	67.89	42.4	49.98	2.05	2.36	0.87
1:50	3.516	0.2574	81.43	30.9	36.44	2.68	3.23	0.83
2:25	5.094	0.258	94.285	20.0	23.585	3.88	5.00	0.78

ED:

Time (min)	Volts	TOC concen-tration (mg/L)	Conduct-ivity (mS/cm)	Ca++ (mg/L)	Ca++ (mol/L)	Cl- (mol/L)	SO4= (mol/L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC not re-moved by ED
0	15	5.179	2.5	72.4	0.00181	0.01026	0.00487	3.95	5.00	1.00
30	15	4.4165	2.5	50.6	0.001265	0.00814	0.00662	3.36	5.00	0.85
60	15	3.7985	2.5	34.8	0.00087	0.00695	0.00729	2.89	5.00	0.73
90	15	3.391	2.5	22.5	0.000563	0.00601	0.00811	2.58	5.00	0.65
120	15	3.1	2.5	14.4	0.00036	0.00527	0.00852	2.36	5.00	0.60
120	15	3.189	2.5	13.3	0.000333	0.00529	0.00867	2.43	5.00	0.62
150	15	3.2675	2.5	8	0.0002	0.00507	0.00860	2.49	5.00	0.63
180	15	3.369	2.5	6.32	0.000158	0.00464	0.00875	2.57	5.00	0.65
210	15	3.095	2.5	2.72	0.000068	0.00419	0.00887	2.36	5.00	0.60
240	15	3.1225	2.5	2.52	0.000063	0.00383	0.00884	2.38	5.00	0.60

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Date 3/14/12
Protocol: RO concentration, maintaining a pH of 7. Add 40.1 g Na_2SO_4 (1.7 g/L), run ED with subsequent Na_2SO_4 addition. ED originally in chloride form.

RO concentration:

Actual time	TOC concen-tration (mg/L)	Permeate TOC concen-tration (mg/L)	Permeate volume (L)	% water remaining	Volume remaining (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining
9:45	1.1192		0	100.0	118.26	1.00	1.00	1.00
10:25	1.4990	0.3991	13.16	88.9	105.1	1.34	1.13	1.19
11:05	1.7771	0.3861	26.65	77.5	91.61	1.59	1.29	1.23
11:45	2.1040	0.3924	39.79	66.4	78.47	1.88	1.51	1.25
12:30	2.5764	0.4601	53.39	54.9	64.87	2.30	1.82	1.26
1:15	2.9203	0.3993	67.89	42.6	50.37	2.61	2.35	1.11
2:00	4.1223	0.4840	82.38	30.3	35.88	3.68	3.30	1.12
2:25	6.0282	0.5004	95.29	19.4	22.97	5.39	5.15	1.05

ED (18.9 g Na_2SO_4 added over time):

Time (min)	Volts	TOC concen-tration (mg/L)	Conduct-ivity (mS/cm)	Ca++ (mg/L)	Ca++ (mol/L)	Cl- (mol/L)	SO4= (mol/L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC not re-moved by ED
0	15	5.8870	3.96	75.4	0.001885	0.00677	0.01361	5.26	5.15	1.00
30	15	5.4450	3.93	52.0	0.0013	0.01378	0.01016	4.87	5.15	0.92
60	15	5.0709	3.93	36.4	0.00091	0.01500	0.00924	4.53	5.15	0.86
90	15	5.0343	3.93	26.6	0.000665	0.01483	0.00943	4.50	5.15	0.86
120	15	4.6699	3.93	20.8	0.00052	0.01407	0.00985	4.17	5.15	0.79
150	15	4.6041	3.93	16.0	0.0004	0.01320	0.01040	4.11	5.15	0.78
180	15	4.5039	3.93	11.1	0.000277	0.01224	0.01120	4.02	5.15	0.77
180	15	4.5082	3.93	11.6	0.000291	0.01229	0.01121	4.03	5.15	0.77
210	15	4.3788	3.93	9.6	0.000239	0.01146	0.01151	3.91	5.15	0.74
240	15	4.2549	3.93	6.9	0.000173	0.01073	0.01204	3.80	5.15	0.72
270	15	4.2732	3.93	6.9	0.000173	0.01005	0.01255	3.82	5.15	0.73

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Date 3/19/12

Protocol: Add 212.3 g Na_2SO_4 (1.8 g/L) to tap water. Run RO and ED simultaneously. pH varies from 7.6 to 8.3. ED originally in chloride form.

Actual time	TOC concen-tration (mg/L)	Permeate TOC concen-tration (mg/L)	Permeate volume (L)	% water remaining	Volume remaining (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining
10:15	1.147		0	100.0	118.66	1.00	1.00	1.00
11:00	1.29	0.2623	13.31	88.8	105.35	1.12	1.13	1.00
11:45	1.4775	0.2738	26.64	77.5	92.02	1.29	1.29	1.00
12:35	1.684	0.2395	40.31	66.0	78.35	1.47	1.51	0.97
1:20	1.946	0.2342	53.38	55.0	65.28	1.70	1.82	0.93
2:10	2.283	0.2583	66.82	43.7	51.84	1.99	2.29	0.87
3:00	2.9275	0.2848	81.29	31.5	37.37	2.55	3.18	0.80
3:57	4.329	0.2829	95.53	19.5	23.13	3.77	5.13	0.74

Actual time	Volts applied	Ca++ (mg/L)	Ca++ (mol/L)	Cl- (mol/L)	SO4= (mol/L)	Conductivity (mS/cm)
10:15	15	14.2	0.000355	0.001667	0.013863	2.78
11:00	15	15.8	0.000395	0.00277	0.014291	3.13
11:45	20	15.6	0.00039	0.003663	0.015356	3.43
12:35	25	15.4	0.000385	0.00421	0.017028	3.80
1:20	27.5	15.8	0.000395	0.004724	0.018946	4.02
2:10	30	15.4	0.000385	0.005431	0.021272	4.08
3:00	30	16.6	0.000415	0.006587	0.025077	4.02
3:57	35	16.6	0.000415	0.008501	0.031615	3.91

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Date 3/21/12

Protocol: RO concentration, maintaining a pH of 7. Add 40.3 g Na_2SO_4 (1.7 g/L), run ED with subsequent Na_2SO_4 addition (10.9 g over 4 hours). ED originally in sulfate form.

RO concentration:

Actual time	TOC concen-tration (mg/L)	Permeate TOC concen-tration (mg/L)	Permeate volume (L)	% water remaining	Volume remaining (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining
10:40	1.0435		0	100.0	118.26	1.00	1.00	1.00
11:15	1.1075	0.2328	13.765	88.4	104.495	1.06	1.13	0.94
11:55	1.257	0.2584	27.665	76.6	90.595	1.20	1.31	0.92
12:40	1.4545	0.2166	40.99	65.3	77.27	1.39	1.53	0.91
1:30	1.8045	0.1918	56.51	52.2	61.75	1.73	1.92	0.90
2:10	2.205	0.1946	69.79	41.0	48.47	2.11	2.44	0.87
2:55	3.1195	0.2019	83.525	29.4	34.735	2.99	3.40	0.88
3:30	4.4505	0.1966	95.17	19.5	23.09	4.26	5.12	0.83

ED (10.9 g Na_2SO_4 added over time):

Time (min)	Volts	TOC concen-tration (mg/L)	Conduct-ivity (mS/cm)	Ca++ (mg/L)	Ca++ (mol/L)	Cl- (mol/L)	SO4= (mol/L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC not re-moved by ED
0	15	4.6677	3.67	62.8	0.00157	0.00432	0.01405	4.47	5.12	1.00
30	15	4.178	3.85	47.2	0.00118	0.00368	0.01670	4.00	5.12	0.90
60	15	3.73	3.96	32	0.0008	0.00335	0.01717	3.57	5.12	0.80
90	15	3.557	4.00	25.8	0.000645	0.00324	0.01818	3.41	5.12	0.76
120	15	3.2068	3.94	20.2	0.000505	0.00297	0.01755	3.07	5.12	0.69
150	15	3.1	3.80	16.6	0.000415	0.00269	0.01649	2.97	5.12	0.66
180	15	2.97	3.68	13.2	0.00033	0.00247	0.01577	2.85	5.12	0.64
210	15	2.7677	3.56	11.8	0.000295	0.00233	0.01547	2.65	5.12	0.59
240	15	2.8225	3.42	9	0.000225	0.00210	0.01467	2.70	5.12	0.60

RO concentration after ED:

Actual time	TOC concen-tration (mg/L)	Permeate TOC concen-tration (mg/L)	Permeate volume (L)	% water remaining	Volume remaining (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining
11:40	5.246		105.31	11.0	12.95	5.03	9.13	0.55
12:48	7.204		109.49	7.4	8.77	6.90	13.48	0.51
12:51	8.176		110.23	6.8	8.03	7.84	14.73	0.53

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Date 3/23/12
Protocol: RO concentration, maintaining a pH of 7. Add 32.9 g NaCl (1.6 g/L), run ED with subsequent NaCl addition (31.0 g over 4 hours). ED originally in chloride form.

RO concentration:

Actual time	TOC concen-tration (mg/L)	Permeate TOC concen-tration (mg/L)	Permeate volume (L)	% water remaining	Volume remaining (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining
10:20	1.210511		0	100.0	118.26	1.00	1.00	1.00
11:05	1.3286	0.1922	14.365	87.9	103.895	1.10	1.14	0.96
11:50	1.5358	0.1334	27.775	76.5	90.485	1.27	1.31	0.97
12:30	1.6154	0.1471	40.725	65.6	77.535	1.33	1.53	0.87
1:15	1.8592	0.1611	53.865	54.5	64.395	1.54	1.84	0.84
5:50	2.416	0.1374	69.835	40.9	48.425	2.00	2.44	0.82
6:35	3.312	0.1813	84.185	28.8	34.075	2.74	3.47	0.79
7:20	4.926	0.1274	97.295	17.7	20.965	4.07	5.64	0.72

ED (31.0 g NaCl added over 4 hours):

Time (min)	Volts	TOC concen-tration (mg/L)	Conduct-ivity (mS/cm)	Ca++ (mg/L)	Ca++ (mol/L)	Cl- (mol/L)	SO4= (mol/L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC not re-moved by ED
0	15	5.548	6.4	74.0	0.00185	0.04423	0.00231	4.58	5.64	1.00
30	15	4.414	7.5	47.5	0.001188	0.05606	0.00219	3.65	5.64	0.80
60	15	3.756	7.23	32.8	0.000819	0.05488	0.00193	3.10	5.64	0.68
90	15	3.61	6.92	24.0	0.0006	0.05259	0.00174	2.98	5.64	0.65
120	15	3.194	6.53	17.3	0.000432	0.04978	0.00152	2.64	5.64	0.58
150	15	3.07	6.31	11.3	0.000281	0.04759	0.00136	2.54	5.64	0.55
180	15	2.776	6.37	7.5	0.000188	0.04799	0.00130	2.29	5.64	0.50
210	15	2.64	6.32	6.0	0.00015	0.04843	0.00118	2.18	5.64	0.48
240	15	2.444	6.3	4.8	0.000119	0.04939	0.00128	2.02	5.64	0.44

RO concentration after ED:

Actual time	TOC concen-tration (mg/L)	Permeate TOC concen-tration (mg/L)	Permeate volume (L)	% water remaining	Volume remaining (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining
6:20	2.6875	0.161	104.995	11.2	13.265	2.22	8.92	0.25
6:40	6.9705		108.545	8.2	9.715	5.76	12.17	0.47

14

Date 3/30/12 – 4/5/12

Protocol: Concentrate 2 tanks around 11.5 times with RO, maintaining a pH around 7. Add 160 g NaCl, run ED. Refill tank, concentrate a total of around 21.5 times. Run ED.

RO concentration tank 1:

Actual time	TOC concen-tration (mg/L)	Permeate TOC concen-tration (mg/L)	Permeate volume (L)	% water remaining	Volume remaining (L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining
2:30	1.0635		0	100.0	118.09	1.00	1.00	1.00
3:15	1.4945	0.2592	13.35	88.7	104.74	1.41	1.13	1.25
4:05	1.7855	0.2319	27.67	76.6	90.42	1.68	1.31	1.29
4:55	2.1745	0.2984	42.745	63.8	75.345	2.04	1.57	1.30
5:45	2.7825	0.2076	58.065	50.8	60.025	2.62	1.97	1.33
6:30	3.4365	0.1748	72.145	38.9	45.945	3.23	2.57	1.26
7:15	4.857	0.2544	86.24	27.0	31.85	4.57	3.71	1.23
8:00	8.115	0.3234	99.925	15.4	18.165	7.63	6.50	1.17
8:20	11.965		105.185	10.9	12.905	11.25	9.15	1.23

V_{total} = 118 L

RO concentration tank 2:

Actual time	TOC concentration* (mg/L)	Permeate volume (L)	% water remain-ing	Volume remaining (L)	TOC concentration factor	Water concentration factor	Fraction of TOC remaining
2:50	1.99	105.185	53.0	118.815	1.87	1.89	0.99
3:35	-	119.395	46.7	104.605	-	2.14	-
4:25	2.63	133.585	40.4	90.415	2.47	2.48	1.00
5:15	-	148.13	33.9	75.87	-	2.95	-
6:05	3.7	162.21	27.6	61.79	3.48	3.63	0.96
10:05	-	176.135	21.4	47.865	-	4.68	-
10:55	6.94	190.465	15.0	33.535	6.53	6.68	0.98
11:45	11.7	204.365	8.8	19.635	11.00	11.41	0.96

V_{total} = 224 L

ED:

Time (min)	Volts applied	TOC concen-tration* (mg/L)	Conduct-ivity (mS/cm)	Ca++ (mg/L)	Ca++ (mol/L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining	Fraction of TOC not removed by ED
0	15	11.7	19.2	156	0.0039	11.00	11.41	0.96	1.00
30	15	10.53	19.6	116	0.0029	9.90	11.41	0.87	0.90
60	15	10.23	19.5	95.2	0.00238	9.62	11.41	0.84	0.87
90	15	10.23	19.5	81.6	0.00204	9.62	11.41	0.84	0.87
150	15	9.33	19	65.6	0.00164	8.77	11.41	0.77	0.80
240	15	8.91	18.7	52.8	0.00132	8.38	11.41	0.73	0.76

RO concentration tank 3:

Actual time	TOC concentration* (mg/L)	Permeate volume (L)	% water remaining	Volume remaining (L)	TOC concentration factor	Water concentration factor	Fraction of TOC remaining
9:10	2.15	204.365	36.5	117.635	2.02	2.74	0.74
10:05	-	218.81	32.0	103.19	-	3.12	-
11:05	3.12	234.035	27.3	87.965	2.93	3.66	0.80
12:05	-	248.625	22.8	73.375	-	4.39	-
1:05	4.6	262.75	18.4	59.25	4.33	5.43	0.80
2:15	-	277.73	13.7	44.27	-	7.27	-
3:25	9.24	293.815	8.8	28.185	8.69	11.42	0.76
5:00	17.61	307.135	4.6	14.865	16.56	21.66	0.76

V_{total} = 322 L

ED:

Time (min)	Volts applied	TOC concen-tration* (mg/L)	Conduct-ivity (mS/cm)	Ca++ (mg/L)	Ca++ (mol/L)	TOC concen-tration factor	Water concen-tration factor	Fraction of TOC remaining	Fraction of TOC not removed by ED
0	15	17.61	20.2	132	0.0033	16.56	21.66	0.76	1.00
30	15	15.99	19.7	140	0.0035	15.04	21.66	0.69	0.91
60	15	16.23	20	126.4	0.00316	15.26	21.66	0.70	0.92
120	15	15.6	20.6	106.4	0.00266	14.67	21.66	0.68	0.89
180	15	14.43	19.4	96	0.0024	13.57	21.66	0.63	0.82
240	15	14.04	18.3	76	0.0019	13.20	21.66	0.61	0.80

*Samples were analyzed by the Illinois State Water Survey (Tekmar Dohrmann Apollo 9000 HS carbon analyzer)