Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.867416

52 (2014) 4603–4611
July

Taylor & Francis
Taylor & Francis Group

Evaluation of ion exchange pretreatment options to decrease fouling of a reverse osmosis membrane

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Received 21 August 2013; Accepted 9 November 2013

ABSTRACT

This research compared pretreatments by anion exchange, cation exchange, and combined ion exchange to a natural groundwater before reverse osmosis (RO) in order to determine which ion exchange process showed the greatest reduction in RO membrane fouling, quantitatively determined by flux decline. It was shown that all ion exchange pretreatments yielded similar rates of flux decline; however, anion exchange pretreated samples yielded overall lower flux meaning it was a less effective pretreatment to reduce fouling. Therefore, the removal of divalent cations, in particular calcium, from a high hardness water by cation exchange showed a greater reduction in fouling of RO compared with the removal of natural organic matter by anion exchange.

Keywords: Ion exchange; Reverse osmosis; Cation exchange; Anion exchange; Membrane fouling; Calcium; Natural organic matter

1. Introduction

Membrane processes for drinking water treatment have gained considerable attention in the last few decades with a market that is expected to continue to grow [1]. As global climate change has led to periods of drought followed by periods of heavy rain, drinking water sources are drastically changing in water quality [2,3]. In order to meet the challenges of these changing water supplies, high pressure membrane systems such as reverse osmosis (RO) are becoming increasingly necessary to produce safe and reliable drinking water [1].

Impacts of changing climate and land use on drinking water sources are not limited to surface water, but can also affect groundwater sources. One such event occurred in Cedar Key, FL, USA, a small town on the gulf coast of north central Florida with groundwater as the source for their drinking water treatment plant. In the summer of 2012, Cedar Key, and north Florida in general, experienced an extended period of drought, which lowered the groundwater level and shifted the salinity boundary. It became apparent that RO would need to be implemented at the treatment plant in order to reduce the total dissolved solids (TDS) to a level that would meet regulations. In less than six months, the RO system was installed at the treatment plant and delivering

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safe drinking water to the community of Cedar Key. Soon after, a wet summer aided in recharging the brackish groundwater with freshwater, and yet the RO unit at the treatment plant continued to experience fouling. Although an antiscalant was used at the plant, it was speculated that inorganic and/or organic fouling was the issue.

Following from the membrane fouling experienced at the full-scale RO plant, this research investigated various ion exchange pretreatment options to reduce fouling of RO membranes. Inorganic contaminant removal to reduce inorganic scaling [4,5] and natural organic matter (NOM) removal to reduce organic fouling [6] can be accomplished with cation exchange and anion exchange, respectively. Combined ion exchange is a novel concept first presented by Apell and Boyer [7], and is considered a feasible option to replace coagulation and lime softening [8], and has the potential to reduce inorganic and organic membrane fouling although it has not been tested directly as a pretreatment before membranes.

Ion exchange and RO membranes are complementary processes in that ion exchange typically releases sodium and chloride when exchanging for more desirable ions in solution such as calcium and NOM, respectively, and RO removes sodium and chloride without significant fouling of the membrane. Other counter ions can also be used for ion exchange including hydrogen ion, hydroxide, potassium, and bicarbonate [9–11], and their effect on the subsequent RO process would need to be considered. For example, cation exchange material in hydrogen ion form and anion exchange material in hydroxide form can be used to desalinate water that contains only sodium and chloride thereby eliminating the need for RO [9]. The situation becomes more complicated with the presence of calcium and NOM in addition to sodium and chloride. It would be difficult for ion exchange or RO alone to treat water that has elevated TDS, calcium, and NOM. Therefore, combined ion exchange has the potential to reduce organic and inorganic fouling of RO, and RO can remove the excess sodium and chloride that is released during combined ion exchange as well as the elevated TDS present in the water that required RO in the first place.

Although the relationship between ion exchange pretreatment and reduction in membrane fouling seems theoretically sound, the literature suggests that it is not straightforward and is even contradictory in some cases. It is clear from the literature that NOM fouls low and high pressure membranes [12,13] and divalent cations such as alkaline earth metals can cause scaling on the surface of the membrane when the localized ion activity product exceeds the solubility product of the mineral [14,15]. It is also clear that adding calcium to water with only NOM as the foulant will increase the fouling due to NOM-Ca complex species [12,16,17]. However, it is not clear if removing NOM as a pretreatment before RO will, in fact, reduce fouling. In theory, NOM can act as an antiscalant by binding to calcium and rendering it less available for precipitation. Likewise, there is very limited research focused on cation exchange alone as a pretreatment to RO. Most importantly, a direct comparison between anion exchange, cation exchange, and combined ion exchange and their impact on RO membrane fouling has never been shown in the literature. As such, this work fills a key gap in the literature on the effectiveness of physical-chemical pretreatment processes to reduce membrane fouling.

The goal of this research was to directly compare the reduction of fouling with the aforementioned ion exchange pretreatment schemes on a low-fouling RO membrane. The specific objectives were: (1) to evaluate permeate flux decline and (2) to investigate changes in water quality due to each ion exchange pretreatment option.

2. Materials and methods

2.1. Test waters

Partially treated groundwater from the Cedar Key Water and Sewer District was used in experiments. The groundwater is characterized by high levels of total iron [3.2 mg/L, unpublished], alkalinity [244 mg/L as $CaCO_3$], hardness [275 mg/L as $CaCO_3$], and dissolved organic carbon (DOC) [5.6 mg/L] [7]. The water treatment process train includes sodium permanganate addition at the well to oxidize iron, magnetic ion exchange (MIEX) process to reduce the DOC concentration, lime softening to reduce hardness, gravity sand filtration, and chlorine disinfection. During the saltwater intrusion event of 2012, the TDS reached more than 1,300 mg/L with a chloride concentration of approximately 600 mg/L. Samples for this work were collected at two locations: (1) after permanganate addition and before MIEX process (i.e. raw water with oxidized iron) and (2) after the MIEX process (i.e. anion exchange pretreated water) and kept at 4˚C until used in experiments.

To simulate the saltwater intrusion event of 2012, ACS grade NaCl was added to the test waters to yield a total chloride concentration of 600 mg/L. The chloride concentration of the untreated groundwater was analyzed by ion chromatography with conductivity detection (Dionex, ICS-3000) according to previously published methods [18] and was determined to be 24 mg/L. Therefore, samples were spiked with 576 mg/L chloride. To simulate cartridge filtration before RO, samples were filtered through a 5-μm polypropylene filter.

2.2. RO experiments

Membrane experiments were conducted using a Sepa CF II membrane cell system. A 3 hp Hydra-Cell diaphragm pump was used to pump the test water to the Sepa cell unit. A refrigerated bath circulator (Neslab RTE-5B) maintained temperature of 23 ± 1˚C of the test water in the tank. A Cole-Parmer differential pressure digital flow meter was attached to the permeate line and a surveillance video camera took digital pictures of the permeate flow every 5 min, transmitted in automated e-mails.

A Dow Filmtec Flat Sheet XLE 40 × 60 RO membrane was used throughout this study. This membrane was chosen because it is considered to be an extra low energy, low fouling membrane. It was stored dry and in the dark until RO membrane coupons were cut. Each experiment was performed with the use of new, preconditioned membrane. These membrane coupons were cut to fit the Sepa CF II membrane cell unit which allows for an effective membrane surface area of 140 cm^2. Coupons were cut from a roll and soaked in deionized (DI) water overnight before each experiment. After soaking, the RO membrane coupons were placed into the Sepa cell unit, inserted into the cell holder, and secured by increasing pressure in the cell holder more than 100 psi (0.69 MPa) than the operating pressure by use of a hydraulic hand pump (Enerpac P-142). DI water was initially pumped through the membrane for 1 h for pre-compaction. Any change in flow as a result of the compaction of the membrane from operating conditions was adjusted for in this initial step. After pre-compaction, a pre-conditioning step was implemented by pumping water with the same ionic strength as the test water through the membrane for 1 h. This was made using ACS grade NaCl and DI water to a chloride concentration of 600 mg/L. Therefore, any fouling that would occur with the test water would not be a result of compaction of the membrane due to pressure or background electrolytes on the surface of the membrane. After pre-compaction and pre-conditioning, test waters were pumped through the membrane overnight. Samples were taken at the initial startup of the test water, then every hour for 6 h after that. Operational pressure was held constant at 200 psi (1.4 MPa).

2.3. Ion exchange pretreatment

The water sample collected after permanganate and before MIEX was used in the RO experiments as is (i.e. no pretreatment) with the addition of NaCl spike, and for the cation exchange pretreatment. The samples "no pretreatment 1" and "no pretreatment 2" were the names given to duplicate experiments that used the same source water. The results for no pretreatment 1 and 2 are shown as individual experiments and not averaged because the results were different due to storage conditions. This may be due to the fact that the "no pretreatment 1" water was the only test water prepared early and subsequently was placed back in the refrigerator until used in the experiment. It is possible that the additional time after the spike in NaCl and filtering changed the water composition resulting in a lower flux than all other experiments. However, the rate at which fouling occurred was very similar. The sample pretreated by cation exchange was treated by rapid mix with a Phipps and Bird jar tester (PB-700) using freshly regenerated Amberlite 200C-Na resin (Dow) with sodium as the mobile counter ion. The method for the regeneration of Amberlite 200C-Na resin is reported in Indarawis and Boyer [18]. After spiking the post-permanganate/before MIEX sample with NaCl, the sample undergoing cation exchange was exposed to a dose of 4 mL/L resin. Volume is not as accurate as mass, therefore resin was dried according to Indarawis and Boyer [18] and sample undergoing cation exchange was dosed dry at an equivalent wet dose of 4 mL/L. The sample collected after the MIEX process was used as the anion exchange pretreated sample and was spiked with NaCl to the desired level. The full-scale condition for anion exchange was an effective resin dose of approximately 1 mL/L of MIEX resin (Orica Watercare) with chloride as the mobile counter ion. The sample collected after the MIEX process was also used as the combined ion exchange pretreated sample (i.e. anion and cation exchange). The sample was spiked with NaCl and treated by Amberlite 200C-Na resin as described above. The composition of the no pretreatment and ion exchange pretreated samples is given in Table 1. The data displayed at time zero in Figs. 3–5 correspond to the same values as the feed water quality in Table 1.

2.4. Analytical methods

Ultraviolet absorbance at 254 nm (UV_{254}) was measured on a Hitachi U-2900 spectrophotometer using a 1-cm quartz cuvette. UV_{254} was used as a surrogate for the DOC concentration. Electrical conductivity was

Table 1
Initial feed water quality

Water type	pH	Conductivity µS/cm	UV_{254} 1/cm
No pretreatment 1	7.8	2,380	0.223
No pretreatment 2	8.0	2,390	0.195
Anion exchange pretreated	8.1	2,540	0.029
Cation exchange pretreated	8.3	2,420	0.718
Anion-cation exchange pretreated	8.2	2,590	0.055

measured using an ECTestr11 + portable electrode (Eutech Instruments). Conductivity was used as a surrogate for the concentration of anions and cations. An Accumet AP71 pH meter with a pH/ATC probe was used to measure pH. The pH meter was calibrated before each use with pH 4, 7, and 10 buffer solutions.

3. Results and discussion

3.1. Flux decline

Fig. 1 shows the flux decline for RO for the two no pretreatment samples, anion exchange, cation exchange, and combined anion exchange and cation exchange, hereafter combined ion exchange. The *y*-axis plots the permeate flux (*J*) normalized to the clean water flux (J_0) recorded during preconditioning. Permeate flux was recorded every 5 min. Small variations in the data were likely to result in fluctuations in the temperature of the water bath or surges from the pump. The general trend of the data indicates that during the first 4 h all of the samples had similar flux behavior, i.e. initially increasing before continuously decreasing. This behavior was largely due to corrected spikes in the initial pressure after starting the experiment. Although each membrane sample was pre-compacted and pre-conditioned for similar ionic strength, erratic increase in the pressure was observed in the first hour of operation. Valves on the membrane system were adjusted during the first hour to maintain constant pressure, thus affecting the initial flux behavior. After 4 h, flux decline showed an approximately linear trend for all samples. Therefore, regression analysis was conducted from hour 4 until hour 9 in order to quantitatively compare the rate of change in permeate flux for each type of pretreatment. Fig. 2 shows the flux decline from hour 4 to hour 9 with regression lines included.

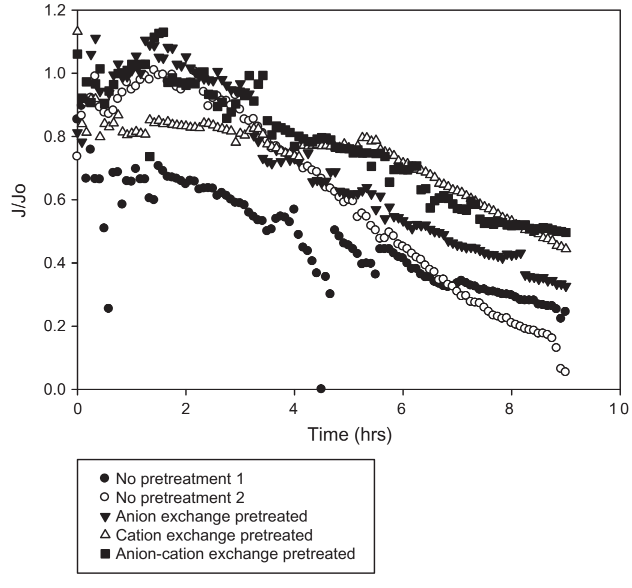

Fig. 1. Normalized flux decline (J/J_0) of no pretreatment and ion exchange pretreatment for reverse osmosis.

Table 2 reports the regression coefficient or *y*-intercept (b_0), regression slope (b_1), and square of the correlation coefficient (r^2) for the linear regression line constructed for each sample. It is clear from the table that the first sample with no pretreatment did not fit

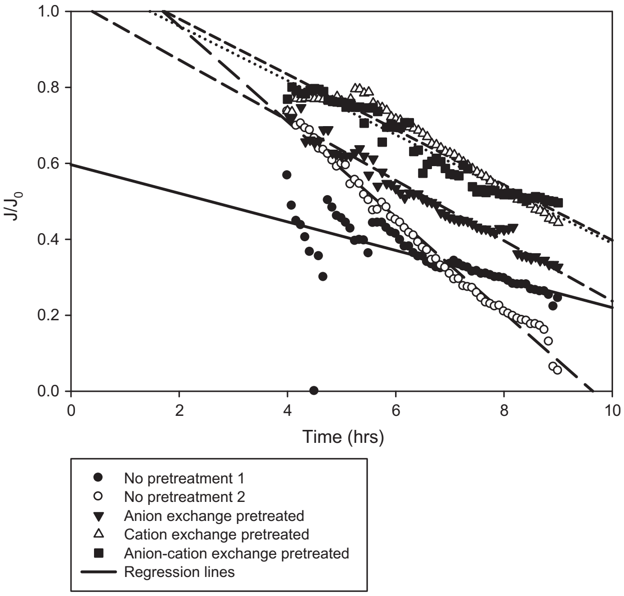

Fig. 2. Normalized flux decline (J/J_0) of no pretreatment and ion exchange pretreatment for RO with regression lines from hour 4 to hour 9 and corresponding regression results in Table 2. Regression lines: no pretreatment 1 (solid), no pretreatment 2 (long dash), anion exchange (medium dash), cation exchange (short dash), and anion-cation exchange (dotted).

Table 2
Linear regression results for trends in normalized flux decline (J/J_0) from hour 4 to hour 9

Water type	b_0	b_1	r^2
No pretreatment 1	0.5963	–0.0376	0.4115
No pretreatment 2	1.214	–0.1259	0.9878
Anion exchange pretreated	1.0313	–0.0794	0.9654
Cation exchange pretreated	1.1260	–0.0729	0.9213
Anion-cation exchange pretreated	1.1044	–0.0715	0.9450

well to the regression equation (r^2 = 0.4115). The data associated with this run shows too much scatter and therefore does not fit well with a linear regression model. The no pretreatment 1 data were not included in further analysis because of the scatter and the second sample with no pretreatment was used as the baseline (r^2 = 0.9878). The slope of the regression line for the no pretreatment 2-data set was –0.1259. Therefore, flux decline for Cedar Key groundwater spiked with NaCl and no pretreatment before RO (other than permanganate addition) from hour 4 until hour 9 yields a decrease in normalized flux of 0.1259 per hour.

Samples pretreated with anion exchange, cation exchange, and combined ion exchange had a very similar rate of decline in flux over time from hour 4 to hour 9 with regression slopes of –0.0794, –0.0729, and –0.0715, respectively. The difference in slope between the no pretreatment 2 and the various ion exchange pretreated samples shows a reduction in flux decline with pretreatment. Although the rate at which flux decline took place for each of the ion exchange pretreatments was the same, there is an initial fouling that occurred with the anion exchange pretreated sample that did not occur with the cation exchange or

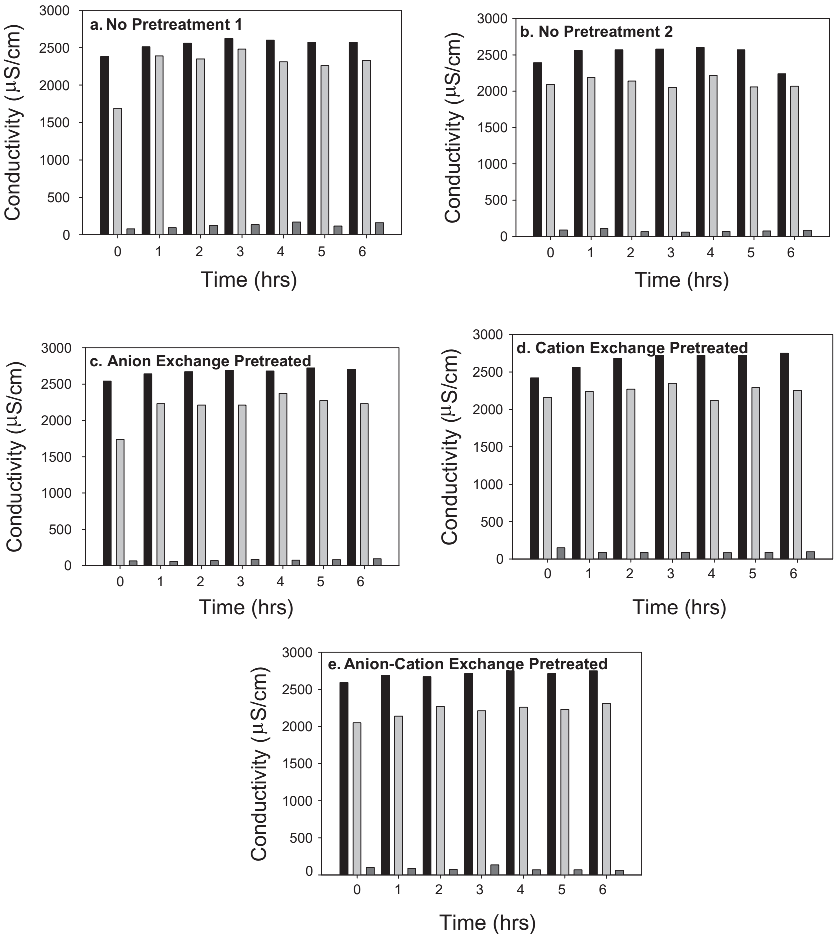

Fig. 3. Conductivity measurements of no pretreatment and ion exchange pretreatment for RO: (a) no pretreatment 1, (b) no pretreatment 2, (c) anion exchange pretreated, (d) cation exchange pretreated, and (e) anion-cation exchange pretreated. Order of bars: Feed water (black), concentrate (light grey), permeate (dark grey).

combined ion exchange pretreated samples. This can be seen in Fig. 2 and Table 2 where the *y*-intercept is lower for anion exchange than either cation exchange or combined ion exchange.

Anion exchange removes a substantial portion of NOM, therefore the remaining ions would predominantly be inorganic cations and fouling would be a result of mineral precipitation (i.e. scaling) from concentration polarization at the surface of the membrane. Because anion exchange removes the negatively charged portion of NOM, the positively charged and neutral portions of NOM can remain after treatment. Examples of these portions of NOM include proteins and polysaccharides. Although the concentration of proteins and polysaccharides is typically low, it is possible that these portions of NOM play a role in fouling of anion exchange pretreated samples. Cation exchange removes a substantial portion of inorganic cations in particular calcium, therefore the remaining ions of concern would be NOM and fouling would be a result of a possible cake formation on the surface of the membrane. Combined ion exchange removes both NOM and inorganic cations, therefore remaining ions of concern would be very minimal in concentration. As such, a shift in the regression line with the anion exchange pretreated sample suggests that inorganic cations precipitating at the surface of the membrane is more significant and problematic than a possible cake layer formed from NOM. In fact, there is no indication of organic fouling with cation exchange pretreated water since it followed almost exactly the same regression line as the combined ion exchange pretreated sample with NOM removed.

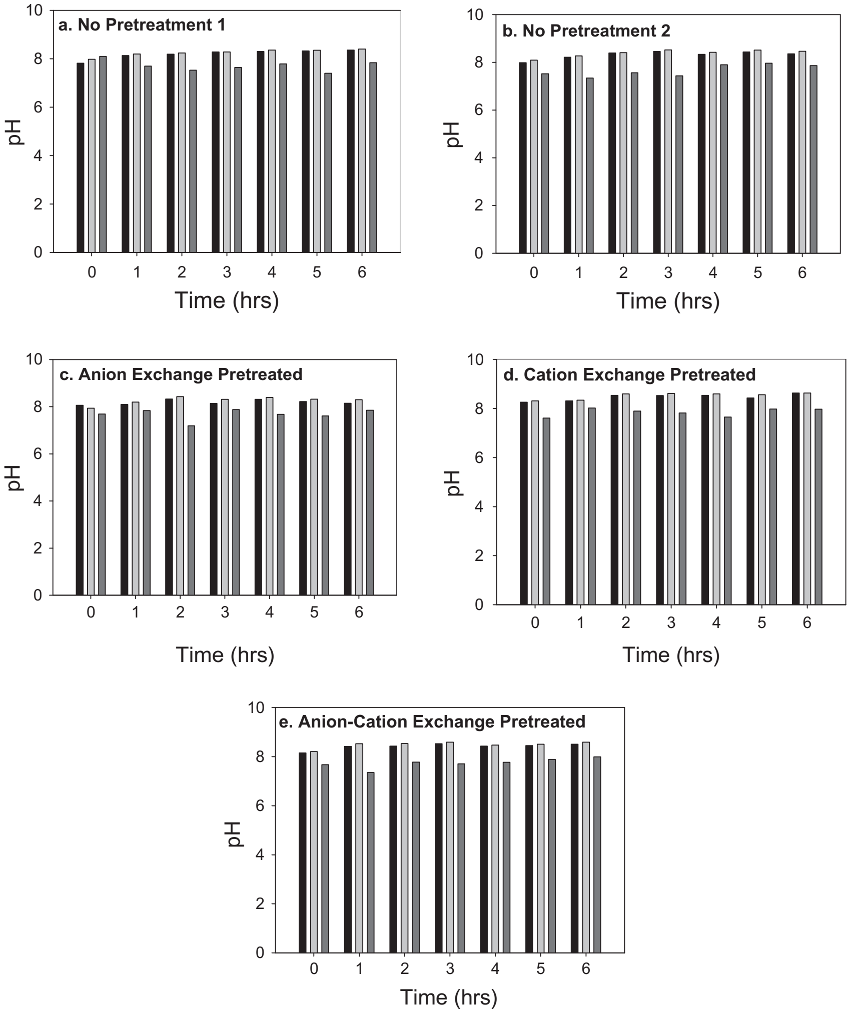

Fig. 4. pH measurements of no pretreatment and ion exchange pretreatment for RO: (a) no pretreatment 1, (b) no pretreatment 2, (c) anion exchange pretreated, (d) cation exchange pretreated, and (e) anion-cation exchange pretreated. Order of bars: Feed water (black), concentrate (light grey), permeate (dark grey).

It is important to note that the results presented here may be different for low hardness water. Cedar Key has high hardness water with calcium as the source of hardness. Previous research with this water has shown precipitation of $CaCO_3$ during anion exchange [8]. This precipitation did not occur during combined ion exchange due to the simultaneous removal of anions and cations. It is possible that $CaCO_3$ is the source of fouling with the anion exchange pretreated water, and that this precipitation would not occur with a low hardness water.

3.2. Changes in water quality

3.2.1. Conductivity and pH

Constant feed water characteristics were important to maintain in all experiments to ensure accurate and reproducible results. Conductivity and pH remained approximately constant in the feed water throughout all experiments (Figs. 3 and 4, respectively) with the ion exchange treated samples having slightly higher (< 10%) conductivity and pH than the no pretreatment samples. Ion exchange using chloride-form anion exchange resin and sodium-form cation exchange is expected to increase the conductivity of the treated water due to release of chloride and sodium. It is not known why there was not a greater increase in the conductivity of the cation exchange treated sample relative to the no pretreatment sample; this is possibly due to the high initial conductivity of the no pretreatment sample. The reduction in conductivity by RO was high for all experiments, as was expected, with reductions between 93 and 98% across all experiments.

Regarding pH, it is important to note that ion exchange pretreatment did not alter the pH with respect to the no pretreatment samples (Fig. 4). The

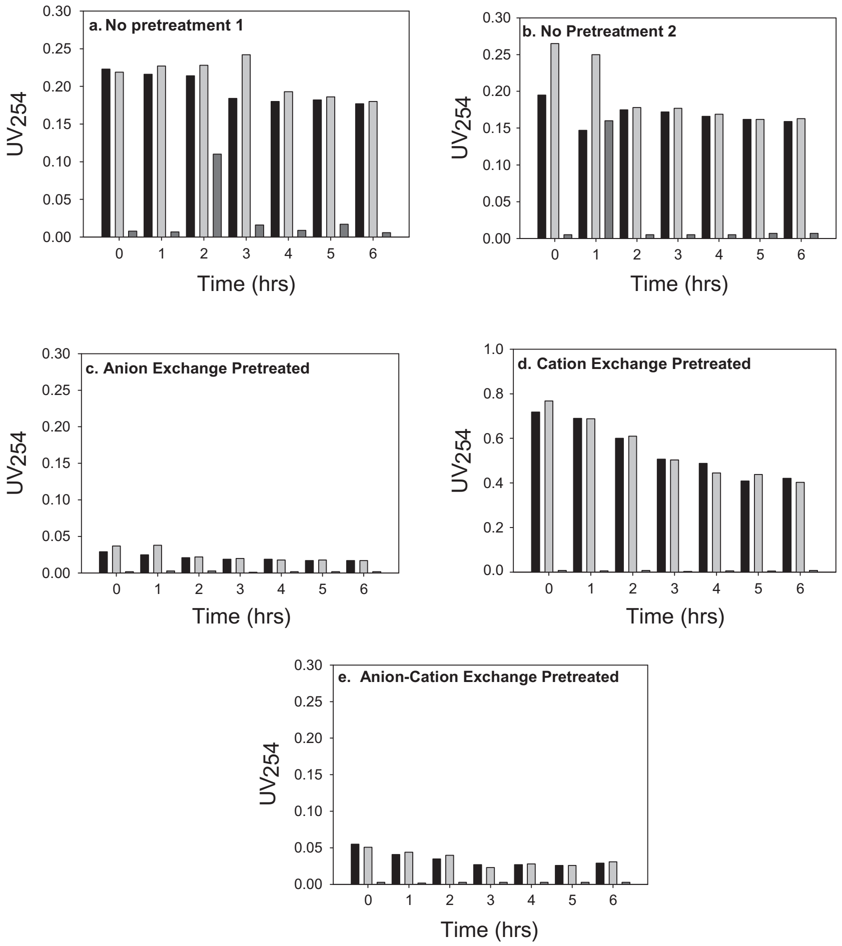

Fig. 5. UV_{254} measurements of no pretreatment and ion exchange pretreatment for RO operation: (a) no pretreatment 1, (b) no pretreatment 2, (c) anion exchange pretreated, (d) cation exchange pretreated, and (e) anion-cation exchange pretreated. Order of bars: Feed water (black), concentrate (light grey), permeate (dark grey).

traditional approach used to remove NOM is coagulation, which lowers the pH, whereas anion exchange did not change the pH. Also, the traditional approach used to remove calcium hardness is lime softening, which increases the pH, whereas cation exchange did not change the pH. For both coagulation and lime softening, pH adjustment by chemical addition is often required depending on the subsequent unit process. The need for chemical additions leads to higher operating costs and more complicated treatment. Thus, combined ion exchange results in a simpler treatment scheme with no chemical addition needed.

3.2.2. UV_{254}

UV_{254} was used as a surrogate measurement for NOM and is shown for feed water, concentrate, and permeate for the different ion exchange pretreatments in combination with RO (Fig. 5). Considering feed water prior to RO, the average reduction in UV_{254} for anion exchange and combined ion exchange relative to no pretreatment was 86 and 74%, respectively. The cation exchange sample had a higher initial UV_{254} absorbance than all other samples, including the two no pretreatment samples (Table 1). Although most samples were decanted from the top of the sample containers, the sample that underwent cation exchange pretreatment was disrupted in the sample container during transport to the jar tester. This mixed any possible iron that had settled to the bottom of the container. As mentioned previously, sodium permanganate is added at the well to oxidize the iron present in the groundwater, and it is possible that the water collected contained iron that was not fully oxidized. It is speculated that during the storage time of the samples, iron oxidation reached completion and precipitated iron settled to the bottom of the container. Although this is speculation, orange precipitates could be seen at the bottom of the sample containers, and the cation exchange pretreated water was slightly orange during the jar test. According to Standard Method (5,910), iron can cause interference with UV absorbance measurement [19]. Therefore, it is possible that the increase in UV absorbance does not reflect an increase in NOM concentration, but rather iron interfering with UV absorbance at that wavelength. Nevertheless, with the increase in UV_{254}, and potentially the presence of iron which is a known RO foulant, the cation exchange sample performed similar to the combined ion exchange sample and yielded less flux decline than the no pretreatment samples (Fig. 2 and Table 2). The reduction in UV_{254} by RO was between 86 and 99% for all samples (except for two samples), and the UV_{254} absorbance of the permeate stream was 0.01 1/cm or less for the majority of samples. Although the RO membrane performed similarly for all types of water, the membrane was likely undergoing greater fouling for the feed waters that had higher UV_{254} absorbance. The UV_{254} absorbance of the concentrate was equal to or higher than the feed water, which is the expected behavior for the concentrate stream. Overall, the UV_{254} data show expected trends with MIEX anion exchange resin and RO achieving high reductions in NOM.

4. Conclusions

- Ion exchange is a viable option for pretreatment to RO membranes.
- Anion exchange, cation exchange, and combined ion exchange showed a decrease in the rate of normalized flux decline than the same water with no pretreatment.
- Although the rate of flux decline was the same for all ion exchange pretreatment options, anion exchange pretreated water exhibited an initial fouling shown by a lower overall flux throughout the experiment compared with cation exchange and combined ion exchange pretreated waters.
- In high hardness waters, inorganic scaling is more severe than organic fouling, thus, indicating a need for cation exchange pretreatment for calcium over anion exchange pretreatment for NOM.

Acknowledgments

KAI was supported by a University of Florida Graduate School Fellowship. We thank the Cedar Key Water and Sewer District for assistance with sample collection. We also thank Jeremy Toms and Avni Solanki for assistance with laboratory experiments.

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