

DESALINATION OF PRODUCED WATER WITH ELECTRODIALYSIS: ION EXCHANGE
MEMBRANE FOULING, SYSTEM PERFORMANCE, AND
FATE OF ORGANIC CONSTITUENTS

by
Amanda S. Yoshino

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Golden, CO

Date _____

Signed: _____

Amanda S. Yoshino

Signed: _____

Dr. Tzahi Y. Cath

Thesis Advisor

Golden, CO

Date _____

Signed: _____

Dr. John McCray

Professor and Department Head

Civil and Environmental Engineering

ABSTRACT

Treatment of oil and gas (O&G) wastewater is a growing practice that increases water resources available for beneficial reuse. Electrodialysis (ED) is an established desalination process with the potential to remove ions from saline produced water (PW), a byproduct of O&G production. However, the current ED literature lacks studies that investigate the fate of organic contaminants during ED treatment using real PW. This work examines ion exchange membrane (IEM) fouling, system performance, and the transport of organic constituents through IEMs during ED treatment of real PW.

A bench-scale ED apparatus was operated in batch mode at constant voltage to desalinate pre-treated PW using two types of IEMs. Pretreatment methods included combinations of biologically active filtration, ultrafiltration, and microfiltration with the intention of progressively increasing IEM exposure to organic matter. Impacts of membrane selection were investigated through measuring stack resistance, current utilization, and loss of water from the diluate due to electro-osmosis. Pristine and fouled IEMs were characterized using environmental scanning electron microscopy (ESEM) and ion exchange capacity measurements.

Fouling layers were not observed using ESEM, though both IEM types experienced decreases in ion exchange capacity. Neosepta IEMs retained a larger proportion of organic matter in the diluate and demonstrated a lower rate of electro-osmosis compared to GE IEMs. Salinity removal was not affected by initial TOC loading in the feed. The mechanism for TOC transport using Neosepta IEMs may be convection, while diffusion is likely the driving force for TOC transport through the GE IEMs. A mass balance of TOC shows that some organic matter was unaccounted for—because excessive membrane fouling was not immediately apparent, this may be evidence that organic matter undergoes oxidation at the anode during ED treatment.

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CHAPTER 1

INTRODUCTION

To meet increasing water demands and reduce potential risks associated with deep well disposal of oil and gas (O&G) wastewater, O&G producers are exploring alternative methods to manage the large volumes of wastewater generated during hydraulic fracturing and production of O&G [1]. The treatment of produced water (PW) for reuse in irrigation may mitigate water stresses in regions that rely on both water-intensive unconventional O&G development and agriculture [1-3]. Water used for irrigation does not require the same quality standards as potable water, which can minimize the costs associated with water treatment [4]. Electrodialysis (ED), a commonly used desalination process, may be a promising method for PW treatment where high quality product water is not required. Specifically, salt in PW will compromise plants and soils, but the organic matter in PW might not harm soil and plants. Several studies have investigated ED as a method of desalination for PW [5, 6], but only few describe the fate of organic constituents during ED treatment. The main objectives of this study were to elucidate the transport of organic constituents through ED membranes and to evaluate the effects of membrane fouling on system performance. ED-treated PW from this study was used in a parallel study to investigate the transport and fate of the organic matter in irrigated crops.

1.1. Background

Hydraulic fracturing is a method used to enhance extraction of hydrocarbons from O&G formations. Hydraulic fracturing fluids (frac fluids)—a mixture of water, sand, and chemical additives—are injected at high pressure into deep subsurface formations. The elevated pressure fractures the rock, creating space for oil, gas, and formation water trapped in pore spaces to flow back through the well when production starts [1]. Water returning to the surface in the first few weeks is referred to as flowback water, while water generated during subsequent O&G production is called PW. Typically, PW is composed of mostly formation brine and contains elevated concentrations of total dissolved solids (TDS), minerals, and organic compounds [7].

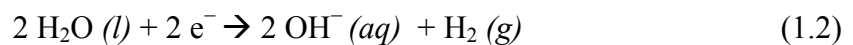
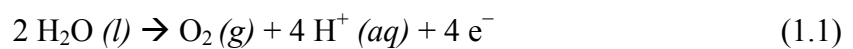
1.2. Treatment and reuse of produced water

High costs associated with the sourcing and trucking of water and disposal of wastewater in the upstream O&G industry has resulted in increasing interest in treatment and reuse of PW. Depending on the distance from the well pad to the reuse site, water treatment and reuse may be more cost-effective than offsite disposal [8]. As a result, water treatment for beneficial reuse is a growing practice in southern and western states such as in Colorado, Texas, Florida, California, and Arizona [9, 10].

PW is a complex waste stream with variable composition, depending on temporal and geologic conditions, but its elevated salinity remains one of the main limitations for treatment and reuse. For example, the salinity of PW ranges from 20,000 to 60,000 mg/L in the Denver-Julesburg (D-J) basin, where our research was conducted [8, 11]. ED, the treatment method employed in this study, can treat saline PW while retaining organic constituents that may not require removal for irrigation reuse.

1.3. Electrodialysis

ED is a membrane separation process in which a direct current electric field is applied to a feed stream, causing anions and cations to migrate toward oppositely charged electrodes [12]. While membrane separation processes such as nanofiltration (NF) or reverse osmosis (RO) use pressure coupled with semi-permeable membranes, ED utilizes electrodes and ion exchange membranes (IEMs) that are largely impermeable to water when operated in the typical cross-flow configuration. Instead, ions pass through alternating cation- and anion-exchange membranes (CEM, AEM), generating a highly saline concentrate stream and a demineralized diluate stream. The IEMs are selectively permeable, allowing the passage of only counter ions. A simplified diagram of an ED membrane stack with ions migrating through the IEMs toward the electrodes is shown in Figure 1.1. An electrode rinse solution is used to remove gases produced through redox reactions at the electrodes [12]. The half reactions shown in equations 1.1 and 1.2 describe the processes occurring at the anode and cathode, respectively [12, 13]:



Several parameters are used to evaluate ED system performance. These include stack resistance, ion exchange capacity (IEC), and salt rejection.

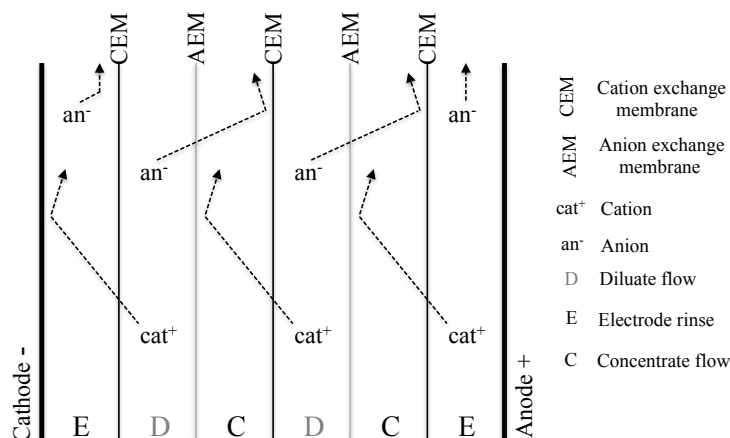


Figure 1.1 Model ED membrane stack configuration, composed of alternating IEMs. The anode attracts negatively charged ions (anions), which cannot pass through CEMs. Similarly, the cathode attracts positively charged ions (cations), which cannot pass through AEMs. Over time, this process generates a high salinity concentrate stream and low salinity diluate stream.

1.3.1. Membrane fouling and stack resistance

Major barriers for further applications of ED include elevated stack resistance and reduced solute flux through the IEMs, both usually associated with membrane fouling [14]. Biological fouling, organic fouling, and inorganic scaling increase the electrical resistance of the membranes and thus the resistance of the membrane stack as a whole [15, 16]. Membrane stack resistance is the sum of the membrane and solution resistances [12, 16]. Membrane fouling obstructs exchange sites, or chemical functional groups on the IEMs, which facilitate transport of counter ions across the membranes. When IEMs become excessively fouled, the impact of the induced electric field on ion migration is diminished [17]. In addition, fouling increases the thickness of the boundary layer where ion depletion may occur, creating a layer of water with high resistivity [12].

AEMs are often disproportionately affected by organic fouling compared to CEMs because the majority of organic matter is negatively charged and may adhere to the AEM [15]. Due to the low electrical mobility of uncharged organic matter in water, organic contaminants are not strongly influenced by the electric field in ED compared to charged ions and can also increase

the resistance of the electrolyte solution itself [17].

Membrane fouling may be either reversible or irreversible depending on whether system performance can be recovered following a cleaning procedure [17]. Chemical cleaning is often conducted “in place” by circulating either an acid or base solution in the diluate flow channels to remove foulants from the membrane surface. Deionized water is then circulated to remove residual acid or base [15]. Compared to base cleaning, acid cleaning has been demonstrated to more effectively reduce membrane resistance and recover ion flux through AEMs [18].

1.4. Previous work

Although ED is an established and effective desalination method for brackish and industrial waters [12, 19-22], recent studies demonstrated that ED is also effective for partial desalination of high salinity feeds when coupled with other treatment methods such as RO [6, 23]. ED has previously been proposed as an onsite treatment method for O&G waste streams. Sirivedhin et al. evaluated treatment of PW for beneficial reuse and focused primarily on ion removal rates, finding that calcium and magnesium were most readily removed from the diluate, followed by potassium and sodium [5]. McGovern et al. established energy requirements for ED treatment of PW and determined that ED is more economical to remove salt from high salinity water compared to low salinity water in terms of cost per unit TDS removed [6]. However, both of these studies used synthetic PW feed solutions comprised of inorganic solutes only and did not investigate transport of organic constituents. To date, no investigation has focused on PW treatment for irrigation reuse or analyzed the transport of organic constituents through IEMs when treating complex waste streams.

1.5. Objectives and scope of work

ED may be an effective process for desalination of PW for irrigation reuse. Highly saline irrigation waters can damage crops when salt in the soil is present in higher concentrations than in the plant roots, causing water to diffuse into the soil rather than into the roots. Saline irrigation waters can yield tissue damage and even crop loss [10, 24]. However, the effect of hydrocarbons on crops has not yet been established. The main objective of this study was to explore the capability of ED to remove salts while retaining organic constituents present in pre-treated PW. We also investigated the effect of organic fouling on system performance using two different sets

of IEMs. The potential of using ED-treated PW for irrigation was investigated in a separate study.

CHAPTER 2

MATERIALS AND METHODS

2.1. PW and solution chemistry

PW was obtained from O&G operators in the D-J Basin in eastern Colorado. Before ED treatment, several pretreatment methods were used to decrease the exposure of the IEMs to organic matter. Biologically active filtration (BAF), microfiltration (MF), and ultrafiltration (UF) were employed for this purpose. BAF is an established treatment method that relies on microorganisms attached to granular activated carbon (GAC) for oxidation of organic matter [25, 26]. The microorganisms degrade a large portion of the organic matter present in the feed water [25-27]. MF and UF are low-pressure membrane filtration processes that rely on size exclusion for removal of particular matter and colloids. MF is a clarification process used to remove particulates and microorganisms larger than 0.1-5 μm while UF uses tighter porous membranes to remove bacteria, viruses, organic macromolecules, colloidal particles, and suspended solids larger than 0.001-0.02 μm [28]. Water quality parameters for the concentrate salt solution (0.25 M NaCl), raw PW from the D-J Basin, and pre-treated PW used in this study are summarized in Table 2.1.

The electrode rinse solution was prepared by dissolving ACS grade (Fisher Scientific) anhydrous Na_2SO_4 in ultrapure water. The integrity test solution and concentrate solution were prepared by mixing ACS-grade NaCl in ultrapure water. The compositions and volumes of the electrode rinse, concentrate, and diluate solutions used for the different experiments are summarized in Table 2.2.

2.2. Bench-scale ED apparatus

A bench-scale ED apparatus was used in the investigation. A photograph and a simplified schematic of the system are shown in Figure 2.1. The apparatus consists of an IEM stack and three 5-L tanks containing the electrode rinse, concentrate, and diluate solutions. The membrane stack is composed of alternating AEMs and CEMs positioned between two electrodes (Figure 1.1). A titanium anode and stainless steel cathode were used as electrodes. Spacers placed between each IEM allowed sufficient space for liquid flow and promoted turbulent flow conditions.

Table 2.1 Average water quality parameters for the concentrate, raw PW, and diluate feed solutions for each experiment

| Parameter | Concentrate | Raw PW | GE IEM Experiments | | | | Neosepta IEM Experiments | | | | |
|-----------------------|-------------|------------|--------------------|-----------|------------|-------|--------------------------|--------|-------|-----------|-------|
| | | | 1-4 | 5-8 | 9-12 | 13 | 1 & 2 | 3 | 4 | 5 & 6 | 7 |
| pH | 6.4 | 6.8±0.3 | 7.64±0.26 | 8.40±0.26 | 7.11±0.05 | 6.62 | 7.81±0.34 | 7.28 | 7.52 | 7.59±0.06 | 6.93 |
| TOC (mg/L) | 0 | 268±105 | 9.7±2.2 | 68.5±3.4 | 171±13 | 179 | 12.4±2.6 | 141 | 109 | 120±7 | 140 |
| Cl (ppm) | 8619 | 15656±4914 | 14531±2882 | 13172±434 | 10492±1714 | 18753 | 10265±1278 | 18720 | 14464 | 20507±807 | 24068 |
| Br (ppm) | BDL | 175±63 | 142±6 | 129±60 | 124±51 | 287 | 181±7 | 243 | 188 | 259±15 | 251 |
| NO ₃ (ppm) | BDL | 29.1±63 | 63±60 | 142±69 | 108±38 | 192 | 134±48 | 37 | 43 | 42±22 | BDL |
| B (ppm) | 51 | 25±8 | BDL | 20±13 | 31±19 | BDL | BDL | 277 | 33 | 3±1 | 15 |
| Ca (ppm) | BDL | 532±265 | 266±59 | 205±200 | 255±163 | 944 | 203±17 | 8561 | 524 | 912±60 | 1002 |
| Mg (ppm) | BDL | 64±38 | 37±5 | 49±9 | 38±7 | 126 | 30±1 | 1212 | 70 | 126±8 | 144 |
| Na (ppm) | 5741 | 7431±2351 | 7352±1035 | 6754±1029 | 5534±778 | 12902 | 6276±1184 | 107469 | 7825 | 12136±601 | 14137 |
| Si (ppm) | BDL | 40±9 | 23±1 | 14±13 | 53±50 | 21 | 14±12 | 165 | 18 | BDL | BDL |

Table 2.2 Initial solutions and volumes used for integrity tests and PW experiments

| | Electrode Rinse Solution | Concentrate Feed | Diluate Feed |
|----------------|--|--------------------|--------------------|
| Integrity Test | 0.25 M Na ₂ SO ₄ , 4L | 0.25 M NaCl, 3.5 L | 0.25 M NaCl, 3.5 L |
| PW Experiment | 0.25 M Na ₂ SO ₄ , 4 L | 0.25 M NaCl, 5 L | PW, 5 L |

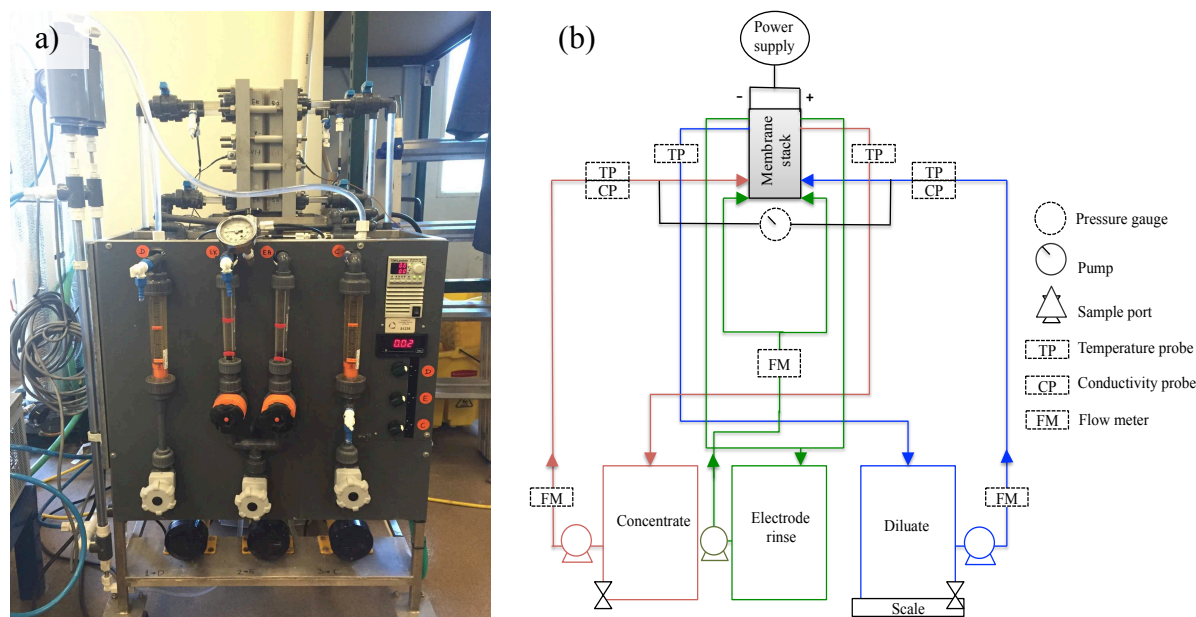


Figure 2.1 (a) a picture of the bench-scale ED apparatus used for experiments and (b) a simplified flow schematic of the system.

The ED apparatus was operated in batch mode by recirculating the concentrate and diluate solutions on the opposite sides of the IEMs. A chiller (Isotemp 3006S, Fisher Scientific) was used to maintain both the diluate and concentrate streams at a constant temperature of 25 ± 1 °C. Magnetically driven centrifugal pumps (Model NH-50PX, Pan World, Ibaraki-ken, Japan) were used to circulate the three streams through their respective hydraulic lines, and toroidal-type electrical conductivity (EC) sensors (Sensorex TCSMA, Garden Grove, CA) were used to measure the EC of the concentrate and diluate streams prior to flowing through the membrane stack. Feed pressures for the concentrate and diluate streams were measured using one 0-30 psi analog pressure gauge (Ashcroft, Burlington, VT) connected through a three-way valve to the three streams. Flow rates were set to 230 liters per hour (L/h) using three separate flow meters (Model SK 72, Georg Fischer, Schaffhausen, Switzerland). The mass of the diluate solution was measured gravimetrically by placing the diluate tank on a digital scale (Model PB5001-S/FACT, Mettler Toledo, Columbus, OH). Mass readings were manually recorded to monitor the decrease in diluate solution mass over time due to electro-osmosis.

2.2.1. System operation

Operational parameters for the ED apparatus and membrane stack are summarized in Table 2.3 and were maintained for all tests. The boundary layer adjacent to the membrane surface was calculated to be approximately 30 μm . It is important to minimize the thickness of the boundary layer in the diluate stream adjacent to the IEM, where the low flow rate can lead to ion-depletion. The rapid rate of demineralization in the boundary layer compared to the well-mixed diluate solution increases stack resistance and decreases the strength of the electric field on ion transport [12, 29, 30].

Table 2.3 Hydraulic parameters of the ED apparatus

| Symbol | Parameter | Equation | Value |
|----------------------------------|--|--|---|
| <i>Hydraulic parameters [31]</i> | | | |
| L | Channel length | | 0.175 m |
| H | Channel height | | 8×10^{-4} m |
| B | Channel width | | 0.12 m |
| a | Half thickness of spacer grid rods | | 0.0002 m |
| ϕ | Inclination angle of grid rods | | 120° |
| λ | Mesh wavelength | | 0.0035 m |
| ε | Spacer porosity | | 0.91 |
| D_H | Hydraulic diameter | $D_H = \frac{8 - \pi \frac{H}{\lambda}}{\frac{4}{B} + \frac{1}{a} + 2\pi(1 - \frac{a}{B})\frac{1}{\lambda}}$ | 0.0011 m |
| <i>Operational parameters</i> | | | |
| ν | Kinematic viscosity | | 1.01×10^{-6} m ² /s |
| D_{Cl} | Diffusion coefficient of chloride in water | | 1.6×10^{-9} m ² /s |
| v | Flow velocity | | 0.15 m/s |
| Q | Volumetric flow rate | | 46 L/hr/cell pair |
| <i>Flow properties</i> | | | |
| Re | Reynolds number | $Re = (D_H v)/\nu$ | 211 |
| Sc | Schmidt number | $Sc = \nu/D_{Cl}$ | 631 |
| Sh | Sherwood number | $Sh = 0.65 Re^{0.875} Sc^{0.25}$ [32] | 35.5 |
| u | Boundary layer | $u = D_H/Sh$ | 30. μm |

2.2.2. Ion exchange membranes (IEM)

Two sets of IEMs were used for the experiments: GE Water (Trevose, PA) and ASTOM Corp. (Tokyo, Japan). A summary of IEMs properties is provided in Table 2.4. Both sets of experiments (using GE Water and ASTOM Corp. IEMs) were conducted with a total active

membrane area of 2050 cm², consisting of six CEMs and five AEMs. IEMs were stored in 0.25 M NaCl whenever the system was not in use.

Table 2.4 IEM manufacturer specifications

| Membrane Manufacturer | IEM | Type | Thickness (mm) | IEC (meq/g) | pH tolerance |
|-----------------------|--------------|-----------------|----------------|-------------|--------------|
| GE Water | AR204 | Homogeneous AEM | 0.6 | 2.4-2.8 | * |
| | CR67 | Homogeneous CEM | 0.6 | 2.1 | * |
| ASTOM Corp. | Neosepta AMX | Homogeneous AEM | 0.16-0.18 | 1.4-1.7 | 0-8 |
| | Neosepta CMX | Homogeneous CEM | 0.17-0.19 | 1.5-1.8 | 0-10 |

* not stated by manufacturer

2.2.3. Supervisory control and data acquisition (SCADA) system

The ED apparatus was operated in constant voltage mode, applying 7 V with a power supply (Model ZUP36-12, TDK-Lambda Corporation, Tokyo, Japan). The system was remotely controlled with LabVIEW (National Instruments, Austin, TX) software. A multifunction DAQ (T7-Pro, LabJack Corporation, Lakewood, CO) was used for data acquisition of temperatures, diluate and concentrate EC, voltage, and current.

2.3. Experimental procedures

2.3.1. PW experiments

Each set of experiments with PW was conducted using increasing concentrations of total organic carbon (TOC) to further challenge the IEMs with exposure to organic matter (Table 2.1). PW pretreatment methods used for the feed water of each experiment are summarized in Table 2.5. A total of 13 experiments were conducted with PW using the GE IEMs. For the first four PW experiments, raw PW was pretreated using a combination of BAF and UF with a final TOC concentration between 5 and 10 mg/L. PW experiments 5 through 8 used raw PW partially pretreated with BAF followed by UF, yielding a final TOC concentration of approximately 70 mg/L. PW experiments 9 through 12 used raw PW partially pretreated with BAF followed by MF (PD-5-934 Polydepth Filter Cartridge, Pentek Filtration, Milwaukee, WI.) with a final TOC concentration of approximately 170 mg/L. And the final experiment (#13) was conducted with raw PW pretreated only with MF, after which the system was cleaned using a 0.01 M HCl solution. Both TDS and TOC concentrations in the last batch were elevated compared to

previous batches (Table 2.1) due to minimal pretreatment (MF only) and salinity variations over time in real PW.

Seven experiments were conducted using the Neosepta IEMs. The first two PW experiments were performed using BAF treated PW followed by UF. The subsequent four experiments were conducted using PW partially pretreated with BAF followed by MF, with an acid cleaning (dilute HCl, pH 2) between the fourth and fifth experiments. The last experiment (#7) was conducted with raw PW pretreated using only MF.

Table 2.5 Experimental design and pretreatment methods. Pretreatment methods were selected to increase the TOC concentrations for each experimental set and to challenge the IEMs with exposure to organic matter. Final experiments (GE #13 and Neosepta #7) tested PW pretreated with only MF.

| IEM used | Experiment | Pretreatment method(s) |
|-----------------------------------|--------------|------------------------|
| GE Water: AR204, CR67 | 1 through 4 | BAF + UF |
| | 5 through 8 | Partial BAF + UF |
| | 9 through 12 | Partial BAF + MF |
| | 13 | MF |
| ASTOM Corp.: Neosepta AMX, CMX | 1 and 2 | BAF + UF |
| | 3 through 6 | Partial BAF + MF |
| | 7 | MF |

At the beginning of each experiment the 5 L diluate tank was filled with PW of varying quality while the concentrate tank was filled with a 0.25 M NaCl solution only. This setup is not representative of a traditional ED operation but was utilized to investigate the transport of organic matter from the PW (diluate flow channels) into the concentrate. PW experiments were conducted with a potential of 7 V across the membrane stack and an initial electrical current of 4 A. Experiments were terminated when the EC of the diluate stream reached 0.5 mS/cm. The terminal EC was established in accordance with general guidelines for irrigation water quality, which cite a maximum EC of 0.75 mS/cm for unlimited irrigation usage [10]. The corresponding TDS for 0.5 mS/cm is approximately 200 mg/L, well below the 500-2000 mg/L concentration recommended by the EPA for irrigation waters [4].

Following each PW experiment and acid cleaning the ED system was rinsed with deionized water to prevent biological accumulation or residual acid in the pipes and pumps. When not in use the ED membrane stack was filled with 0.25 M NaCl solution.

2.3.2. Integrity tests

An integrity test was conducted prior to and following each PW experiment to identify any changes in salt removal rates and system resistance, and to determine whether membrane fouling hinders system performance. During the integrity tests NaCl solution was used on both the concentrate and diluate sides of the IEMs. Constant flow rate (230 L/h), pressure (35 kPa (5 psi)), and temperature (25 ± 1 °C) were maintained throughout the integrity tests, while the conductivity in the concentrate and the diluate tanks continually changed and were monitored continuously using the SCADA system. Each integrity test was conducted at a constant voltage of 7 V and initial current of 4 A, and was terminated when the EC of the diluate stream reached 0.5 mS/cm.

2.3.3. IEM cleaning procedure

A 0.01 M HCl acid solution was used to regenerate the IEMs after fouling occurred, indicated by increased membrane stack resistance. The GE IEMs were cleaned after the final PW experiment, while the Neosepta IEMs were cleaned following the fourth PW experiment. Cleanings were conducted by circulating three liters of 0.01 M HCl (pH 2) in the diluate flow channels for one hour at a flow rate of 230 L/h. The concentrate (0.25 M NaCl) and rinsing (0.25 M Na₂SO₄) streams were recirculated at the same flow rate. After the system was drained, the diluate and concentrate channels were rinsed with deionized water for one hour, and then stored in 0.25 M NaCl solutions.

2.4. Water sample collection, preparation, and analysis

2.4.1. Sample collection

3-4 samples were collected from the concentrate and diluate streams during experiments with PW. In addition to initial and final samples, 40 mL solutions were typically collected when a decrease in current was first observed and when the current decreased at the fastest rate. During IEM cleanings, samples were collected from the diluate (0.01 M HCl) at the beginning and end of each cleaning. Samples were collected from the diluate and concentrate before cleaning, and from the diluate after cleaning. Each sample collected during experiments was stored in the refrigerator (4 °C) before preparation for analysis. Milli-Q water was used for all dilutions, which were sample-specific depending on TDS concentration.

2.4.2. Chemical analysis

TOC analysis was performed using the combustion catalytic oxidation method on a Shimadzu TOC-LCSH system (Shimadzu Corporation, Kyoto, Japan). Anion concentrations were determined with ion chromatography (Thermo Scientific ICS-900, Dionex, Sunnyvale, CA) and cation concentrations were measured using an inductively coupled plasma (ICP) optical emission method (Optima 5300 DV ICP-OES, PerkinElmer Inc., Waltham, MA).

Liquid chromatography coupled with mass spectrometry (LC/MS/MS-QTOF) was used to determine the molecular weight distribution for organic matter in each flow channel for the last experiment conducted with each type of IEM (GE #13, Neosepta #7). Initial and final diluate samples in addition to final concentrate samples were collected and analyzed using an AB SCIEX TripleTOF 5600 with a Shimadzu CBM-20A System Controller equipped with two LC-30AD binary pumps and a CTO-30A Column Oven (Kyoto, Japan). An HPLC reversed phase Luna 3 μm C18(2) 100 Å, LC Column 150 x 4.6 mm (Phenomenex Torrance, CA) column was used to separate the analytes and was maintained at a constant temperature of 40 °C. The injected sample volume was analyzed in positive mode. Data analysis was conducted using Analyst software PeaKView (SCIEX, Framingham, MA) using non-target analysis.

2.5. Membrane characterization

Physiochemical membrane characteristics were analyzed for pristine and fouled GE and Neosepta AEMs. Fouling was evaluated using an environmental scanning electron microscope (SEM). Changes in IEM functional groups for pristine and fouled IEMs were determined through ion exchange capacity experiments.

2.5.1. Scanning electron microscopy (SEM)

Pristine and fouled IEMs were visually inspected for damage and fouling using an FEI Quanta 600 environmental scanning electron microscope (ESEM) (FEI, Hillsboro, OR). 25 cm² membrane coupons were cut from pristine and fouled GE and Neosepta AEMs. The AEM and CEM coupons were collected from the IEMs in the middle of the stack. Samples were desiccated for 24 hours and subsequently gold-sputtered (Technic Hummer VI, Cranston, RI) before being examined with the ESEM. In combination with ESEM, energy dispersive spectroscopy (EDS) was used to evaluate the content of inorganic deposits on the IEM surface.

2.5.2. Ion exchange capacity (IEC)

Ion exchange capacity is a fundamental physical property of IEMs that correlates directly to desalination efficiency. A decrease in ion exchange capacity signifies a decrease in the number of functional groups per membrane mass available to facilitate ion transport [33]. Changes in IEM functional groups were analyzed using IC in accordance with previous methodology [12, 34, 35].

Pristine and fouled membrane coupons (900 mm²) were soaked in a 0.1 M NaCl solution for 24 hours to ensure that the electrostatic bonds on the membrane were composed of predominantly sodium for CEMs and predominantly chloride for AEMs. CEMs were then soaked in 100 mL of 0.1 KCl solution to exchange the cations on the membrane to mostly potassium. After the membranes soaked for one hour, the 0.1 M KCl solution was replenished to maintain a strong concentration gradient of potassium between the solution and the CEM. Finally, the 0.1 M KCl solution was replenished a second time and the CEMs were soaked for 24 hours to ensure that all sodium ions were replaced with potassium ions. One sample for ICP analysis was collected from each KCl solution before replenishment in order to analyze the total concentration of sodium ions replaced on the CEM.

Similarly, after soaking AEMs in 0.1 M NaCl, the AEMs were soaked in a 100 mL of 0.1 M NaNO₃ solution to exchange the chloride ions on the AEMs with nitrate (NO₃⁻) ions. Following one hour of soaking, the 0.1 M NaNO₃ solution was replenished and the membranes were soaked for another hour. Finally, the 0.1 M NaNO₃ solution was replenished again and the membranes were soaked for 24 hours. One sample was collected for IC analysis from each NaNO₃ solution prior to replenishment of the solution to evaluate the total concentration of chloride ions replaced on the AEM. Solution pH was monitored to ensure that hydrogen and hydroxide ions were not transferred from the AEM instead of sodium and chloride.

CHAPTER 3 RESULTS AND DISCUSSION

3.1. Stack resistance and diluate electrical conductivity

3.1.1. PW experiments

Membrane stack resistance rises as salts are removed from the diluate channels during ED treatment. The salt concentration in the diluate and concentrate flow channels was monitored by continuous EC measurements, as shown in Figure 3.1a for the GE IEMs and Figure 3.1b for the Neosepta IEMs. The GE membrane stack resistance for PW experiments 2, 5, 9, and 13 are shown for experiments conducted with a variety of feed TOC concentrations (Table 2.5). While membrane resistance increased throughout each experiment, the overall stack resistance did not increase between experiments 2 and 13. Stack resistance between these experiments remained almost identical, even at low diluate EC when membrane resistance becomes more relevant to overall stack resistance [16]. During experiment 9 the membrane stack exhibited anomalously elevated resistance, likely due to the spike in feed TOC concentration and exposure to organic foulants that could deposit on the IEM surface.

Between experiments 2 and 4 with the Neosepta IEMs, membrane stack resistance increased from 4.0 to 5.2 Ω at a diluate EC of 3 mS/cm. A dilute acid cleaning was performed after experiment 4, which decreased the stack resistance to 3.7 Ω at a diluate EC of 3 mS/cm (below the 4 Ω observed in experiment 2). Experiment 7 was conducted with raw PW pretreated with MF only. During that experiment the stack resistance increased to just over 4 Ω at a diluate EC of 3 mS/cm. The increase in stack resistance during the experiments was caused by either deposition of organic foulants on the IEM or increased solution resistance due to uncharged organic constituents in the pretreated PW (initial diluate) [17].

Because membrane electrical resistance is inversely proportional to membrane thickness, the inherent resistance of the GE IEMs was expected to be slightly elevated compared to that of the Neosepta IEMs [12, 16]. While the resistance of the GE IEMs was indeed higher than that of the Neosepta IEMs, the stack resistance during experiments with GE IEMs did not increase substantially after 13 cycles of PW treatment.

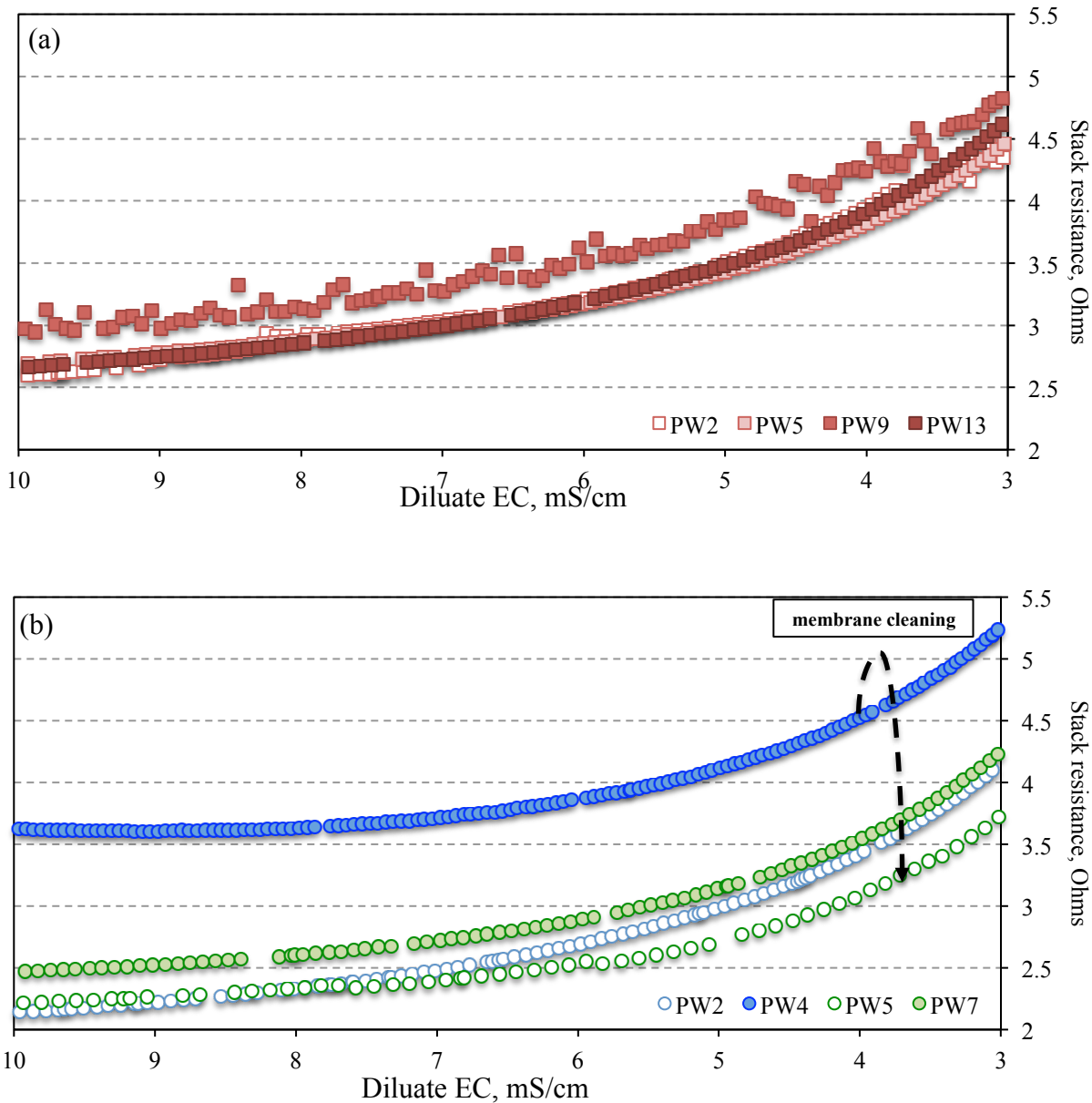


Figure 3.1 Stack resistance change with diluate EC during PW experiments conducted with (a) the GE IEMs and (b) the Neosepta IEMs. As expected for both IEM types, stack resistance increases when fewer ions are available to conduct current in the diluate channel. Following equilibration, the GE IEMs did not show increased resistance, even after 13 PW experiments. The stack resistance for the Neosepta IEMs increased substantially between experiments 2 and 7, demonstrating a high fouling propensity.

3.1.2. Effect of PW exposure on IEM performance

An integrity tests was conducted between each PW experiment to isolate changes in stack resistance and desalting rates following IEM exposure to foulants. Each integrity test was conducted using 0.25 M Na_2SO_4 in the electrode rinse solution and initially 0.25 M NaCl on both

the concentrate and diluate sides of the IEMs. Stack resistance as a function of diluate EC for representative integrity tests are shown in Figure 3.2. Black lines show the resistance for each integrity test at a corresponding diluate EC of 6 mS/cm. Stack resistance increased after 13 experiments conducted with the GE IEMs (Figure 3.2a). The system cleaning (details in Sec. 2.3.3) was partially effective in reducing stack resistance (integrity test 12 vs. integrity test 13). The cleaning partially regenerated the IEM surface, lowering the stack resistance to 3.2 Ω , but was unable to restore to the original resistance of 2.7 Ω at 6 mS/cm. For integrity tests conducted with the Neosepta IEMs, stack resistance increased from 2.7 to 3 Ω at 6 mS/cm after 3 PW experiments (integrity test 1 to integrity test 4.) System cleaning had little effect on stack resistance and may have even temporarily impaired system performance (integrity test 6). Stack resistance decreased to approximately 2.5 Ω at 6 mS/cm after three more experiments conducted with pretreated PW (integrity test 9). Although it is not immediately clear why the stack resistance would decrease following multiple cycles of PW exposure, it may be that constituents adhering to the Neosepta IEMs increase solute flux rather than blocking IEM functional groups.

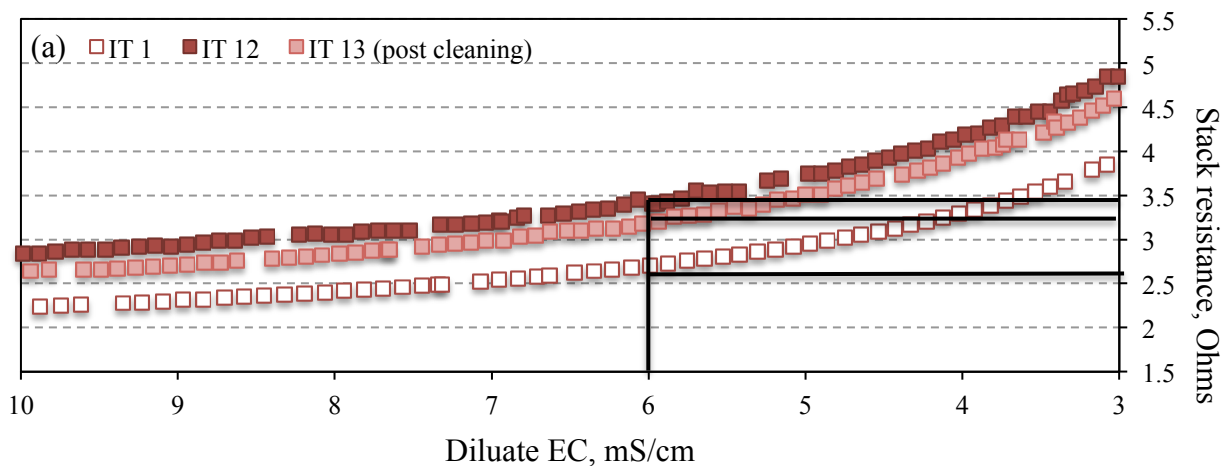


Figure 3.2 Change in stack resistance for integrity tests conducted with (a) GE IEMs (red squares) and (b) Neosepta IEMs (blue circles). Black lines show resistance values for each integrity test at a diluate EC of 6 mS/cm. Stack resistance increased following PW treatments. A dilute acid cleaning effectively decreased GE membrane stack resistance but temporarily increased the Neosepta membrane stack resistance at low diluate EC (integrity test 5 vs. integrity test 6). Surprisingly, stack resistance decreased after subsequent PW treatments (integrity test 9).

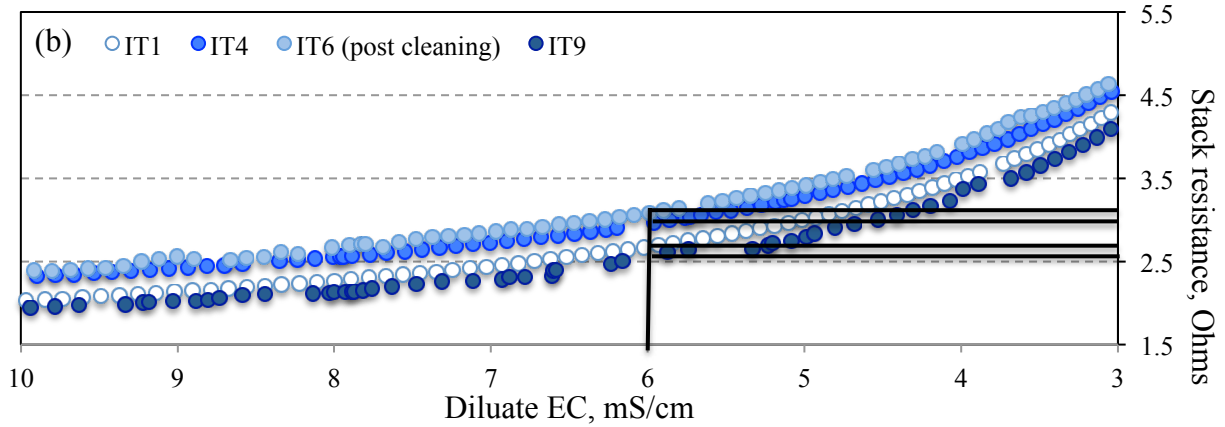


Figure 3.2: Continued

Current efficiency (Figure 3.3b) was slightly lower at higher measured currents (when diluate EC was elevated) and slightly higher at lower measured currents toward the end of the experiments. Thus, current efficiency varied substantially, ranging from 35 to 82% for the Neosepta IEMs and 39 to 65% for the GE IEMs. These values fall within the range of current efficiency previously calculated for ED systems [35, 36, 38]. Overall, PW experiments conducted with the Neosepta IEMs demonstrated higher current efficiency rates than those conducted using the GE IEMs.

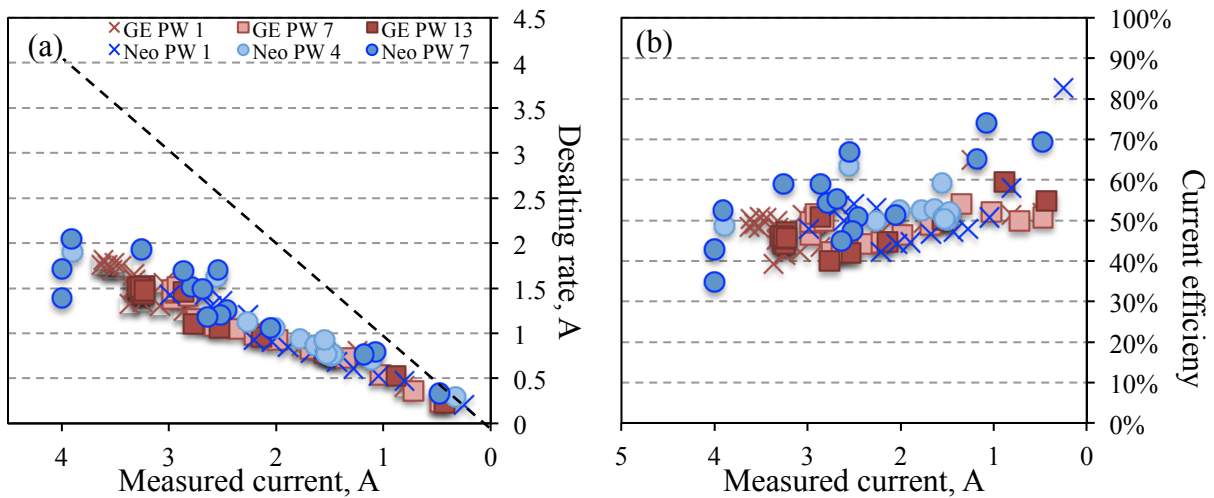


Figure 3.3 (a) Desalting rate and (b) current efficiency as a function of measured current. The desalting rate falls below the theoretical 100% black-dashed line, confirming that a portion of the current is utilized for processes apart from ion removal. Rates do not substantially differ between initial and final PW experiments. As measured current decreases (due to ion depletion in the diluate), desalting rates decrease. The Neosepta IEMs just slightly outperform the GE IEMs.

3.1.3. Electro-osmosis of water from the diluate to the concentrate

In general, water is transported from the diluate into the concentrate during ED treatment by either osmotic pressure or by electro-osmotic transport via ion hydration shells [39]. The hydration shells of sodium, magnesium, and chloride contain approximately 4, 15, and 8 moles of water per mole of ion, respectively. These hydration shells act as the mechanism for water transfer from the diluate into the concentrate [12, 37, 40]. As previously demonstrated by Han et al., electro-osmosis in ED increases with the presence of specific salts such as $MgCl_2$ and $NaCl$ [37]. Thus, the more selective the membrane is, the less water it will let through.

The ratio of water transfer to salt transfer as a function of (a) PW experiment length and (b) experiment number are shown in Figure 3.4. While a strong correlation does not exist between the PW experiment length and ratio of water to salt transfer, experiments with the Neosepta IEMs consistently yielded a lower ratio (3 to 4 compared to 4.5 to 6.5 for the GE IEMs) (Figure 3.4a). Thus, more moles of water were transferred from the diluate to the concentrate per mole salt for the GE IEMs. The ratio of water to salt transfer was not dependent on PW experiment number (and thus TOC loading) (Figure 3.4b).

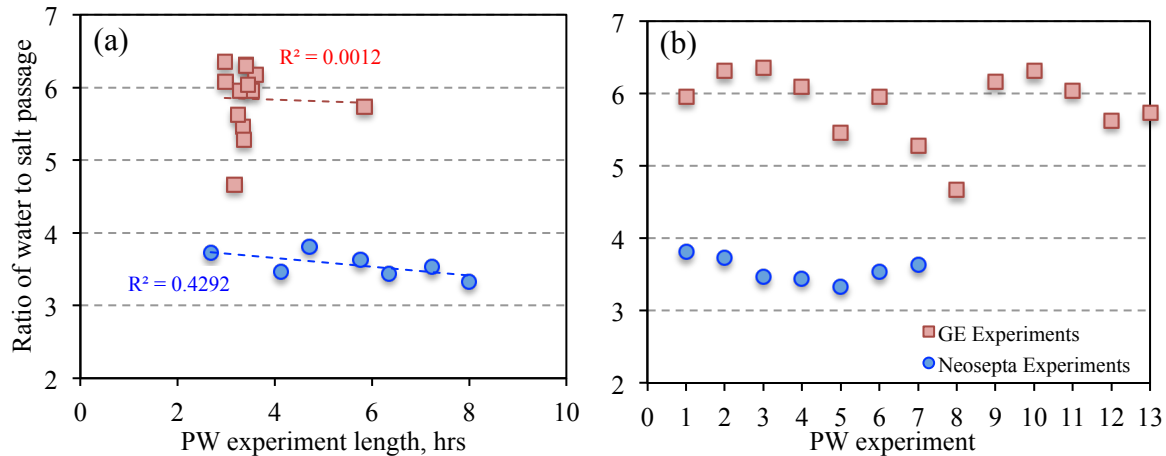


Figure 3.4 Ratio of water mass lost (g) to salt passage (g) from diluate into concentrate as a function of (a) PW experiment length and (b) PW experiment number. The ratio of water to salt passage was relatively constant for both the Neosepta and the GE IEMs regardless of PW experiment length. The GE IEMs consistently yielded a higher ratio of water to salt passage.

Total water loss from the diluate as a function of (a) integrity test length and (b) variance in integrity test lengths between each PW experiment is shown in Figure 3.5. Like during PW

experiments, integrity test results also demonstrate that water transport is relatively constant for both the Neosepta and the GE IEMs, with the Neosepta IEMs retaining more water in the diluate compared to the GE IEMs. On average, 313±22 g of water was transferred into the diluate during integrity tests of the GE IEMs, accounting for 6.27±0.44% of the initial diluate volume. 200±18 g of water were transported during integrity tests with the Neosepta IEMs, accounting for 4±0.37% of the initial diluate volume. For integrity tests, water transfer appears to be associated exclusively with salt transfer (i.e., via ion hydration shells) because the water transfer was relatively constant.

The length of each integrity test conducted using the GE IEMs increased slightly after each exposure to TOC during PW experiments. GE IEMs likely experienced some amount of fouling or blocking of functional groups that led to decreased solute flux and longer integrity tests. The length of each integrity tests with Neosepta IEMs unpredictably decreased slightly after each PW experiment. It is not immediately clear why the lengths of the integrity tests decreased, but one explanation could be that constituents adhering to the IEMs actually promoted ion transport and increased system efficiency, as previously discussed (Section 3.1.2).

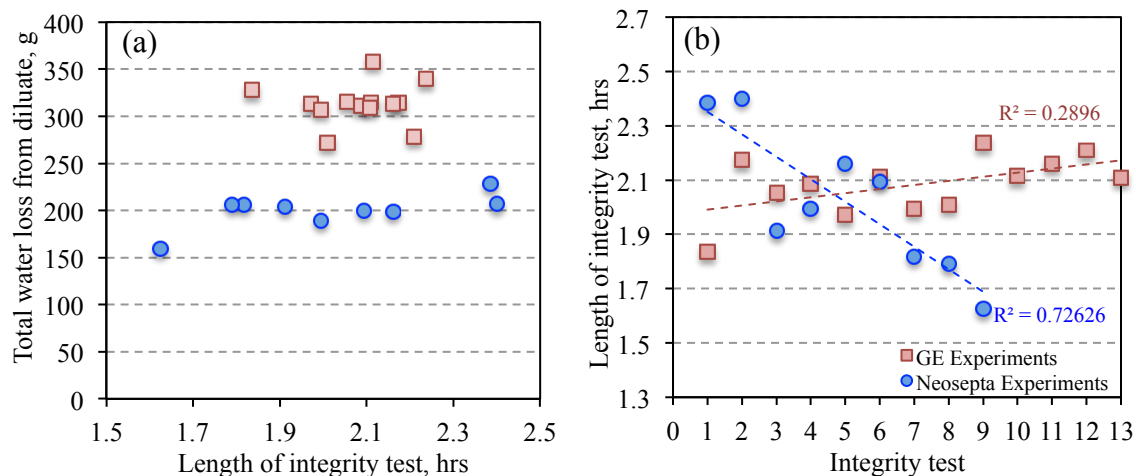


Figure 3.5 Total water loss as a function of (a) integrity test length and (b) integrity test length variations. Total water loss from the diluate had little variation for both the Neosepta and the GE IEMs, indicating that the mechanism for water transfer is associated with salt transport during integrity tests. On average, the Neosepta IEMs lost approximately 4% of the initial diluate volume, whereas the GE IEMs lost just over 6% of the initial diluate volume. While the GE IEMs did not show a clear variation in integrity test length over time, the lengths of integrity test with the Neosepta IEMs decreased following additional PW experiments.

3.2. System performance

3.2.1. Salt mass balance and solution chemistry

Although each batch of PW treated in this study originated from the same well, initial EC values differed depending on the stage of well development. Therefore, relative percent concentrations were calculated to show removal rates and preferential ion transfer. The relative percent of main cation concentrations present in the diluate over time for experiments conducted with the GE and the Neosepta IEMs are shown in Figure 3.6. The relative percent concentration of sodium decreased substantially from over 90% in the initial diluate to 50-80% following ED treatment. Sodium accounted for a smaller relative percentage of the final diluate for experiments conducted with both IEM types because sodium was readily removed during ED treatment while other ions were difficult to remove and become enriched in the diluate. ED also readily removed calcium as well as bromate (though at concentrations <1% in the feed water), confirming ion removal results from previous studies [5]. Silicon and boron were persistent in the diluate, accounting for as much as 13% and 35% of the final cation composition in the final diluate, respectively. Previous studies also found boron removal to be problematic. Boron removal depends heavily on solution pH, with elevated removal up to 97% at a pH range of 9 to 10.5 [41-43]. At pH 8.5, separation of boron by ED did not occur at all when using Neosepta IEMs [44]. Similarly, removal of silicon is also dependent on pH with optimal removal around 9.5 when silicon is in the anion form and can migrate into the concentrate [45]. Because silicon and boron are uncharged at the near-neutral pH of the pretreated PW feed in the present study, they were not heavily influenced by the electric field.

Chloride was the dominant anion in the diluate, consistently accounting for over 94% of the total anion composition in the diluate throughout all but one experiment, indicating that enrichment of specific anions in the diluate was not as prevalent as enrichment of cations. Neosepta experiment 3 demonstrated anomalous enrichment of bromide and thus contained only 86% relative concentration of chloride. Relative percent concentrations of sulfate accounted for approximately 0.4% of the total ion composition during all experiments with both IEM types. Sirivedhin, et al. treated PW with varying levels of TDS [5]. Three voltage settings were applied and ion concentrations were measured to identify which were readily removed and those that were more persistent.

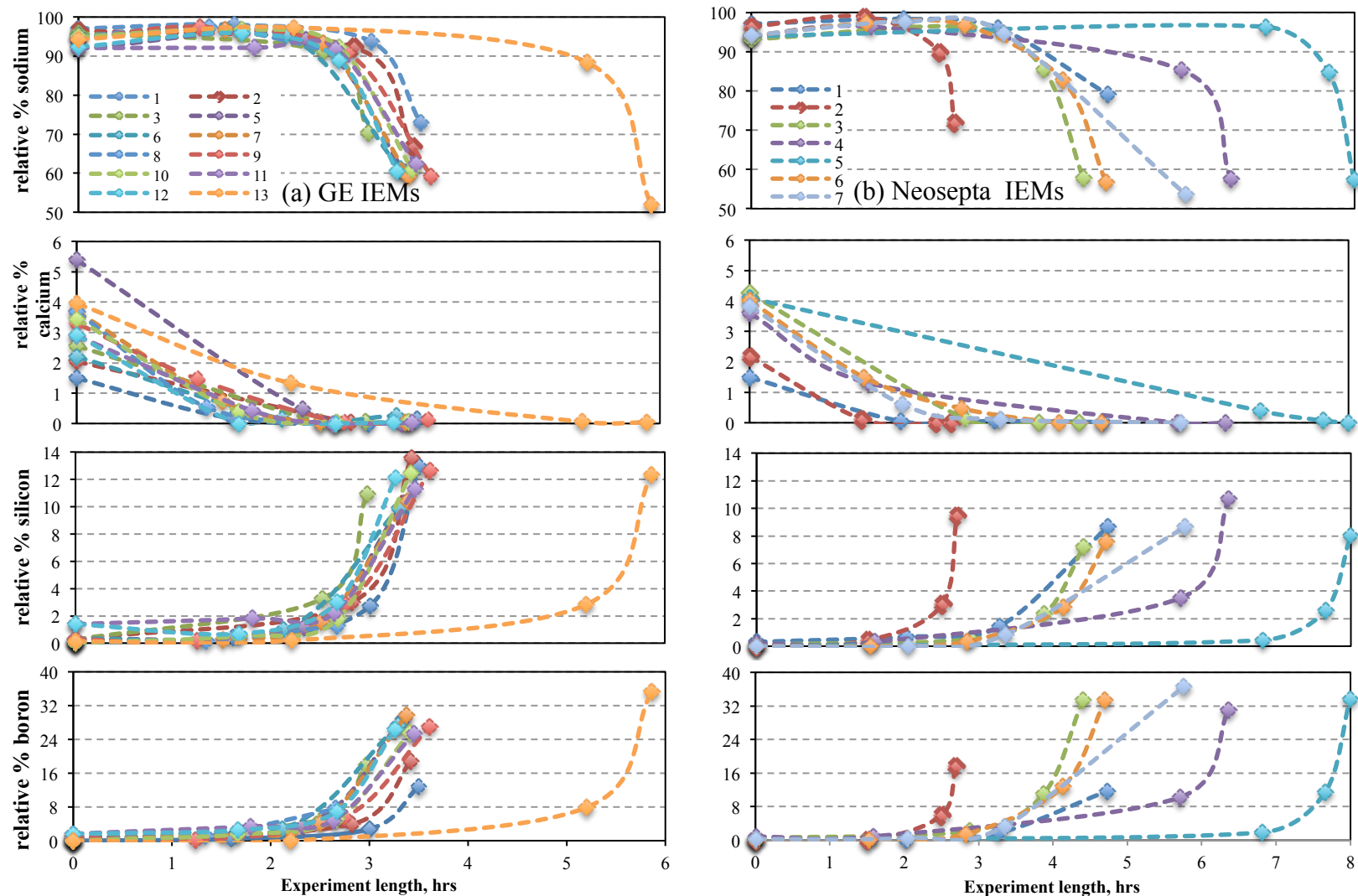


Figure 3.6. Sodium, calcium, silicon, and boron relative percent concentrations in diluate over time for experiments conducted with (a) the GE IEMs and (b) the Neosepta IEMs. Removal trends are similar for both IEM types; ED readily removed calcium and sodium but silicon and boron were persistent in the diluate, comprising up to 13% and 35% of the diluate cation composition, respectively.

Using Neosepta IEMs, their results demonstrated that calcium and magnesium were the most readily removed cations, followed by potassium and sodium. Sulfate was the most readily removed anion, followed by bicarbonate and chloride. As previously discussed by Farrell, et al., selectivity is approximately the same for monovalent and divalent ions [46]. The results in the present study confirmed these removal rates and did not demonstrate disparate selectivity for monovalent ions compared to multivalent ions.

3.2.2. TOC mass balance

For this experimental setup, TOC originated exclusively from the diluate PW feed stream. During ED treatment, TOC mass may stay in the diluate, diffuse into the concentrate, adhere to the IEM, or undergo oxidation. In order for oxidation to occur, TOC has to be transported from the diluate compartment into the electrode rinse solution in contact with the anode. Oxidation of TOC may also occur in the saline-poor boundary layer where hydroxide ions form due to water splitting.

Previous studies established that organic movement in the ED process is mainly diffusion-driven in the presence of salt, regardless of the voltage applied [47]. Additionally, the presence of NaCl has been shown to increase the rate of neutral organic solute transport through IEMs. This occurs as ions fill their hydration shells, leading to relative dehydration of the organic solutes. This dehydration causes smaller organic solute size (i.e., organic solutes without full hydration shells) and increases their convective flux through the IEMs [37]. Previous research characterized organic foulants in ED as organic matter that is either too large to permeate the IEM and thus deposits on the IEM surface, or as small organic matter that can penetrate the IEMs. Both types of organic foulants increase the electrical resistance of the membrane due to low electric mobility [22, 48] and formation of an additional resistance layer on the membrane.

TOC retention in the diluate and passage into the concentrate during experiments with the GE IEMs are summarized in Table 3.1 and shown in Figure 3.7. Over the course of 13 PW experiments, a maximum of 42% of the feed TOC was retained in the diluate. 26 to 61% of the initial TOC mass permeated the IEMs, transferring from the diluate into the concentrate. Step-wise increases in initial diluate TOC concentrations were used to further challenge the IEMs with exposure to organic matter (Figure 3.7). While TOC partitioning varied for each experiment, the percent TOC retained in the diluate remained between 30 and 42%. GE experiment 13 was

conducted with raw PW pretreated with MF only, exposing the IEMs to substantially higher concentrations of organic constituents and particulate matter. However, only 23% of the initial TOC mass passed into the concentrate. Fouling or TOC oxidation may account for the large portion of initial TOC that was unaccounted for following treatment (i.e., neither present in the final diluate nor the final concentrate).

Table 3.1 TOC mass balance for the GE IEMs. 30-42% of the initial TOC mass was retained in the diluate, while 23-61% of the initial TOC mass transferred into the concentrate flow channel

| Pre-treatment method(s) | Exp. # | Initial TOC mass (mg) | Final TOC mass (mg) | Percent retention of TOC mass | Average final TOC mass in concentrate (mg) | Percent TOC mass passed to concentrate |
|-------------------------|--------|-----------------------|---------------------|-------------------------------|--|--|
| BAF + UF | 1 | 12.2 | 3.9 | 32% | 3.8 | 26% |
| | 2 | 52.4 | 19.2 | 37% | 23.9 | 46% |
| | 3 | 43.1 | 14.0 | 32% | 25.0 | 53% |
| | 4 | 36.5 | 13.8 | 38% | 16.3 | 45% |
| Partial BAF + UF | 5 | 328 | 119 | 36% | 145 | 44% |
| | 6 | 328 | 136 | 42% | 175 | 53% |
| | 7 | 357 | 141 | 39% | 188 | 53% |
| | 8 | 357 | 113 | 32% | 191 | 53% |
| Partial BAF + MF | 9 | 947 | 304 | 32% | 468 | 49% |
| | 10 | 859 | 269 | 31% | 433 | 50% |
| | 11 | 811 | 243 | 30% | 426 | 52% |
| MF | 12 | 811 | 245 | 30% | 497 | 61% |
| | 13 | 895 | 379 | 42% | 212 | 23% |

TOC retention in the diluate and transfer into the concentrate during experiments with the Neosepta IEMs are summarized in Table 3.2 and shown in Figure 3.8. TOC retention rates ranged from 49 to 76% and did not show a strong correlation to feed water quality. Between 32 and 52% of the TOC mass permeated the Neosepta IEMs and transferred into the concentrate stream. Due to low resolution for experiments 1 and 2 conducted with low feed TOC concentrations, the percent retention and percent TOC mass transported into the concentrate appear to exceed 100%. Compared to the GE IEMs, the Neosepta IEMs retained a larger percent of TOC (30 to 42%, and 49 to 76%, respectively.) However, a larger percent of organic constituents were unaccounted for after the experiments conducted with the GE IEMs and MF-treated PW (experiment 13).

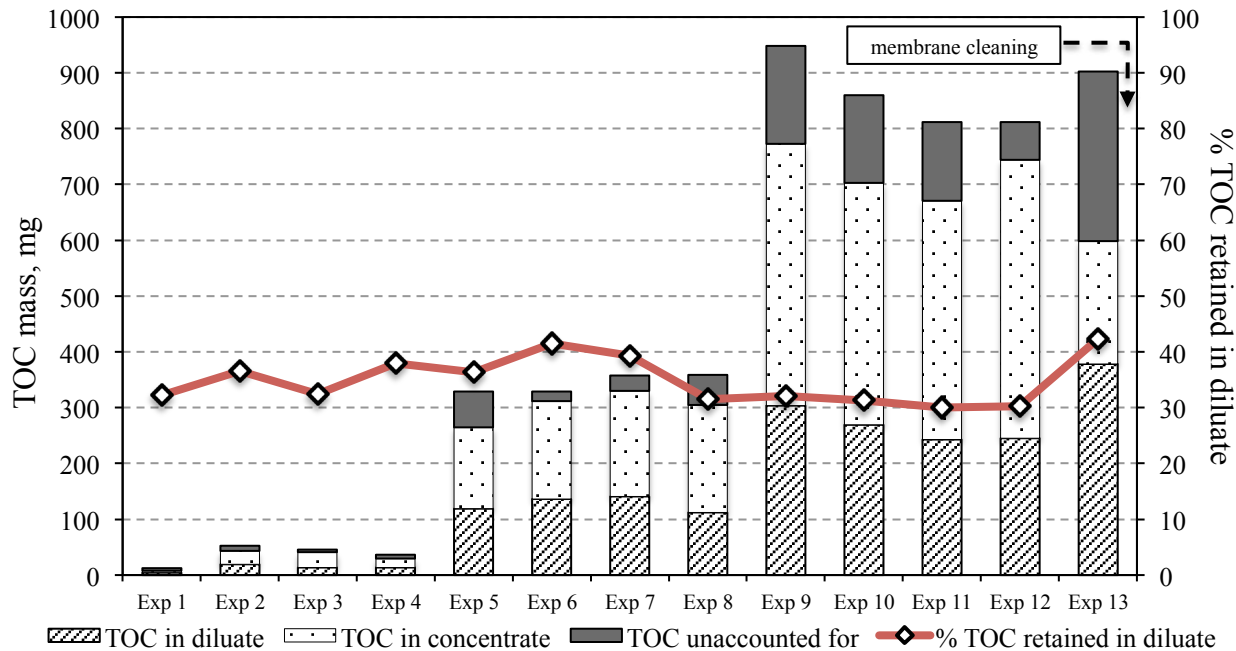


Figure 3.7 TOC mass balance for experiments conducted with the GE IEMs. Initial TOC mass was increased after each set of four experiments to discern changes in the fate of organic constituents. The mass of TOC unaccounted for increased with increasing initial TOC mass in the system. The overall percent retention of TOC was lower than for the Neosepta IEMs (Figure 3.8) (30-42% compared to 49-76%).

A smaller portion of TOC mass was unaccounted for during experiment 4 compared to experiment 3, indicating that adsorption sites may have saturated from exposure to elevated concentrations of organic matter. Following membrane cleaning, foulants may have adhered to the IEMs during experiment 5 when exposed to a more pristine surface once again. Only a very small portion of TOC mass was unaccounted for (1.2 mg) following experiment 7, which was conducted using raw PW pretreated using only MF. Again, this phenomenon may be caused by decreased availability of IEM adsorption sites. For similar experimental conditions conducted with the GE IEMs (experiment 13), a substantial portion of TOC was unaccounted for.

Vanoppen, et al. established that diffusion is the primary driving force for passage of organic matter through the IEMs from the diluate into the concentrate [49]. Experiments were conducted using a diluate composed of trace organic constituents (TOrcs) and NaCl as well as TOrcs alone. Results showed that TOC was less likely to permeate the IEMs when the feed water contained elevated concentrations of NaCl due to preferential transport of ions due to size, charge, and concentration [49]. This conflicts with previous studies that indicate increased transport of neutral organic constituents in the presence of salt [37]. In a later study conducted by

Vanoppen, et al., Fujifilm Type I IEMs were used to differentiate between the effect of diffusive and electromigrative forces on organic matter. Experiments were conducted with constant applied current or no applied current. Results demonstrated no disparity in transport of organic matter whether or not current was applied through the membrane stack [47]. In the present study, feed waters contained both high TDS as well as high concentrations of TOC (leading to increased diffusive driving forces and higher TOC transport). Therefore, TOC transport trends were difficult to elucidate in the pretreated PW complex waste stream.

Table 3.2 TOC mass balance for the Neosepta IEMs. 49-76% of the initial TOC mass was retained in the diluate, while 32-52% of the initial TOC mass transferred into the concentrate stream

| Pretreatment method(s) | Experiment | Initial diluate TOC (mg) | Final diluate TOC (mg) | Percent retention of TOC mass in diluate | Average final TOC in concentrate (mg) | Percent TOC mass passed to concentrate |
|------------------------|------------|--------------------------|------------------------|--|---------------------------------------|--|
| BAF + UF | 1 | 70.9 | 43.7 | 62% | 36.6 | 52% |
| | 2 | 52.6 | 39.8 | 76% | 16.7 | 32% |
| | 3 | 705 | 390 | 55% | 234 | 33% |
| Partial BAF + MF | 4 | 537 | 306 | 57% | 217 | 40% |
| | 5 | 627 | 305 | 49% | 201 | 32% |
| | 6 | 578 | 282 | 49% | 202 | 35% |
| MF | 7 | 702 | 421 | 60% | 280 | 40% |

The TOC removed from the diluate as a function of water mass transported from the diluate is shown in Figure 3.9. There is a weak positive correlation ($R^2 = 0.6283$) between the percent TOC removed and the water mass transferred for the experiments conducted with the Neosepta IEMs. Han, et al. investigated the influence of salt on the transfer of neutral organic solutes through IEMs, identifying both diffusion and convection due to electro-osmosis as driving forces for organic solute transfer [37]. The positive correlation between percent TOC removal and water loss during experiments with the Neosepta IEMs indicates that TOC mass may be transported with water through the Neosepta IEMs. However, water transfer and percent TOC removal remain mostly constant during experiments with the GE IEMs, apart from one outlier, indicating that the driving force for TOC transfer may be diffusion. The one outlier was GE experiment 13, which contained elevated salinity compared to other experiments with the GE IEMs (Table 2.1).

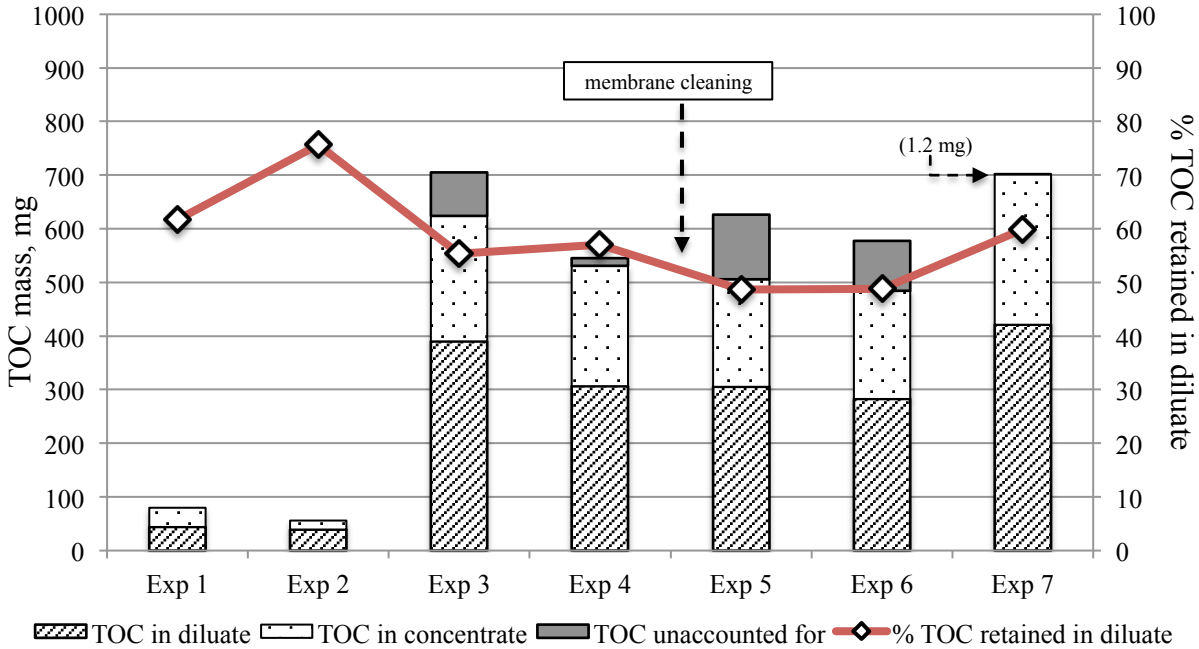


Figure 3.8 TOC mass balance for experiments conducted using the Neosepta IEMs. Initial TOC mass was set to be higher after the first two experiments. The GE IEMs demonstrated increased mass of TOC unaccounted for as feed TOC mass increased (Figure 3.7). However, there was no consistent pattern of TOC mass unaccounted for over the course of the experiments conducted with the Neosepta IEMs.

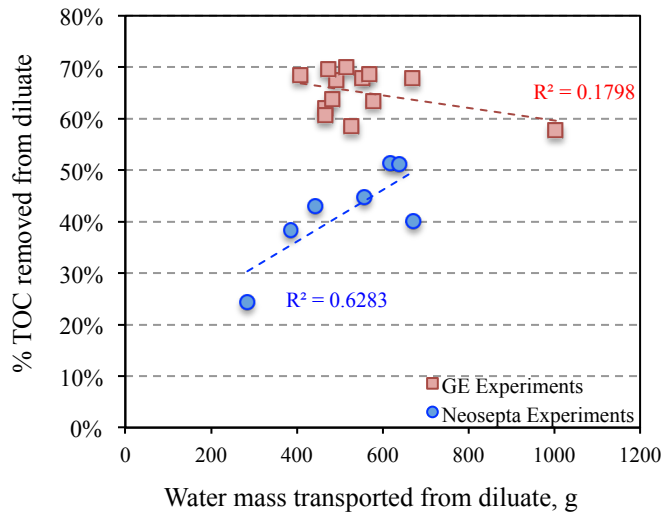


Figure 3.9 TOC removal as a function of water transport. There was a slight correlation between the percent removal of TOC and the water mass lost during experiments conducted with the Neosepta IEMs, possibly pointing to convection due to electro-osmosis as a driving force for organic solute transfer in PW experiments. The lack of strong correlation between water transport and TOC removal for experiments conducted with the GE IEMs points to diffusion as the dominant force for TOC transport.

3.2.3. Liquid chromatography-mass spectrometry (LC/MS/MS-QTOF) data analysis

Samples for LC/MS/MS-QTOF analysis were collected during experiments conducted with PW pretreated with MF only (GE #13 and Neosepta #7, see Table 2.1 for details). Initial diluate samples were raw PW pretreated with MF only and final diluate samples consisted of ED-treated water. Final concentrate samples were collected from the concentrate channel at the end of ED treatment and contained organic constituents (and inorganic solutes) that permeated the IEMs.

The mass distribution for organic constituents identified with LC/MS/MS is shown in Figure 3.10 for (a) experiments with the GE IEMs and (b) experiments with the Neosepta IEMs. A method blank was used as a control for both sets of experiments. For both sets of experiments, several constituents not detected in the initial diluate samples were detected in the final diluate. It is possible that these constituents are breakdown products of other organic compounds in the initial diluate. While specific compounds were not identified, the most prevalent organic constituents to permeate the IEMs into the concentrate had a molecular weight of 300-400 Daltons (Da).

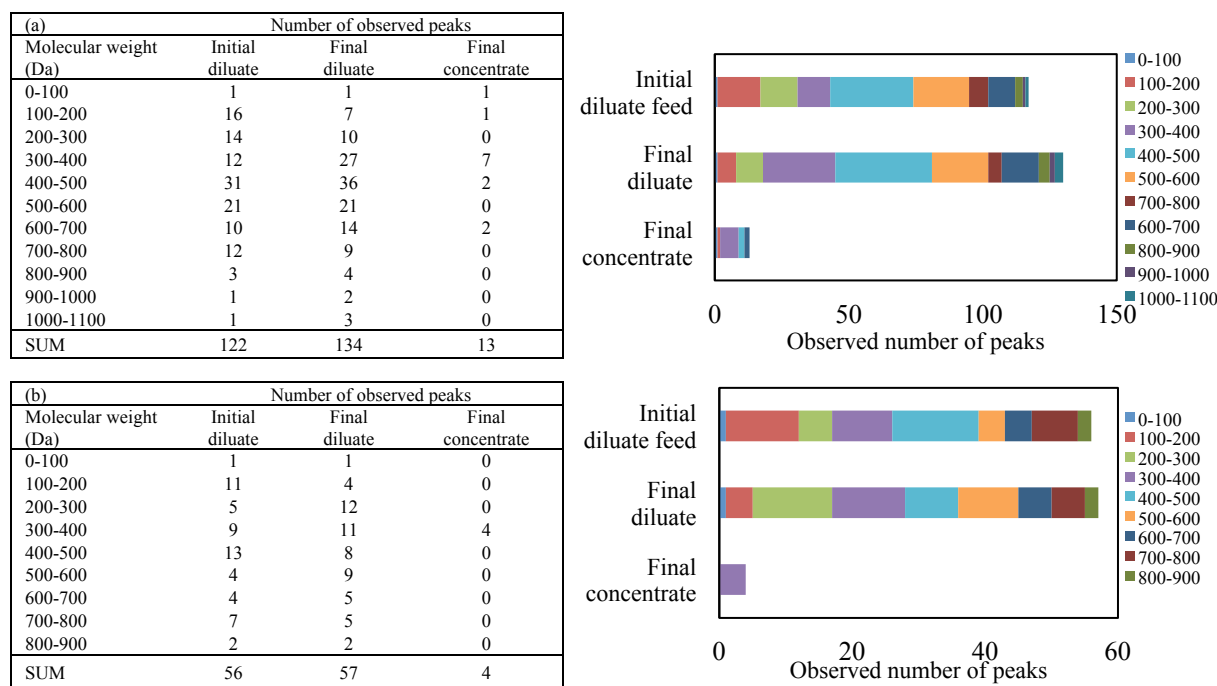


Figure 3.10 Mass distribution charts for (a) experiments with the GE IEMs and (b) Neosepta IEMs. Several constituents not identified in the initial diluate feeds were detected in the final diluate, possibly indicating that organic constituents degraded during ED treatment. Organic constituents with molecular weight of 300-400 Da were the most abundant constituents to permeate the IEMs into the concentrate.

Heat maps depicting peak intensity for organic constituents identified in experiment 7 with the Neosepta IEMs and experiment 13 with the GE IEMs are shown in Figure 3.11. Lighter and more hydrophilic constituents are associated with the left side of the heat map (shorter lengths of time) while heavier and more hydrophobic constituents are generally appear on the right side of the heat map (longer lengths of time). The method blank (representative of water used for dilutions) used in conjunction with the GE IEMs samples showed peaks between 37 and 40 minutes. The heat maps indicate that organic constituents passing through the IEMs into the concentrate are predominantly hydrophobic, while more hydrophilic constituents were more likely to remain in the diluate.

Based on its molecular mass and presence in hydraulic fracturing fluid, the peak observed around 31 minutes in the initial Neosepta diluate sample (Figure 3.11b) may represent benzalkonium chloride, a biocide and cationic surfactant often used in hydraulic fracturing fluid [50]. This constituent was not detected in the final diluate or concentrate samples.

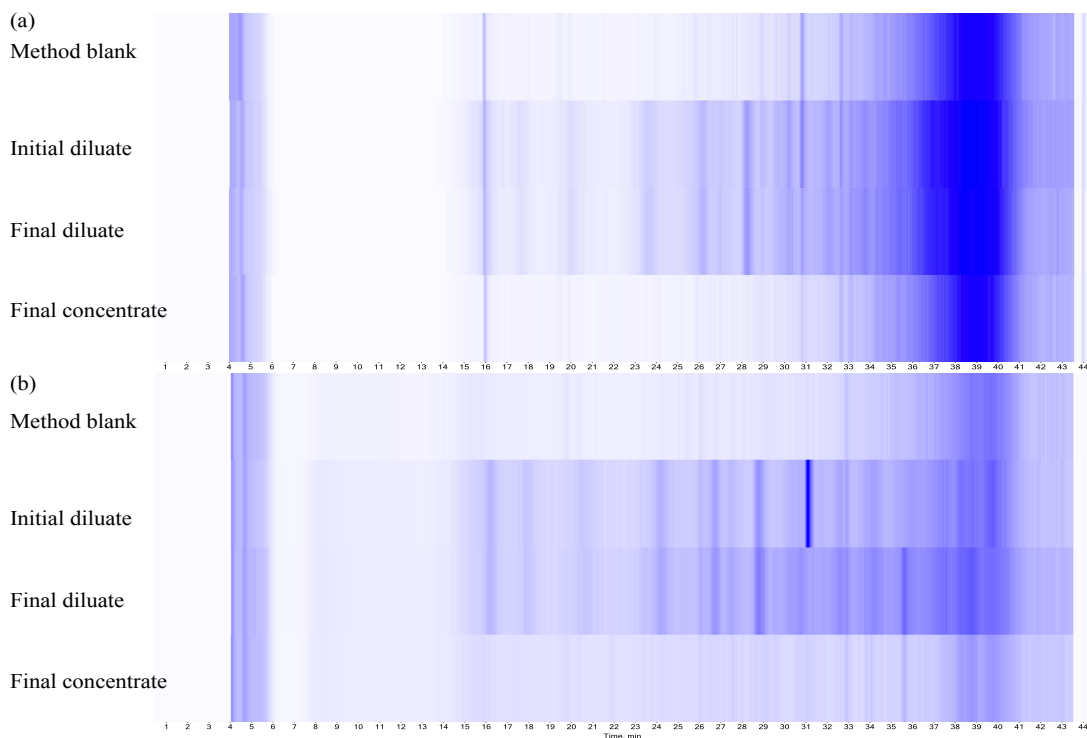


Figure 3.11 Heat map showing initial and final diluate samples, final concentrate samples, and method blanks used for (a) experiment 13 with the GE IEMs and (b) experiment 7 with the Neosepta IEMs, both conducted using PW pretreated with MF only.

3.3. IEM characterization using ESEM and ion exchange capacity

ESEM analysis and ion exchange capacity tests were performed to compare physicochemical properties and visible characteristics of pristine and fouled IEMs. ESEM provided a qualitative examination of the AEMs while ion exchange capacity tests quantified changes in IEM functional groups following exposure to pretreated PW.

3.3.1. ESEM analysis

Pristine and fouled AEMs were examined for fouling and defects using ESEM. ESEM micrographs of the pristine and fouled surfaces for GE and Neosepta AEMs are shown in Figure 3.12. Because many organic constituents are negatively charged and more likely to adhere to the AEM surface, AEMs were the focus of the ESEM analysis [15]. The underlying support layer of the GE IEMs cracked during desiccation, as seen in both the pristine and fouled micrographs (Figure 3.12a and 3.12b), but surface-level defects were not observed on either the fouled GE AR204 or Neosepta AMX membranes. The inorganic content of the white lines on the IEM surfaces (Figure 3.12b) were evaluated using energy dispersive spectroscopy (EDS). The surface of the fouled GE AR204 contained calcium while the surface of the fouled Neosepta AMX (Figure 3.12d) contained barium. The apparent lack of fouling or major inorganic deposits on the IEM surfaces may be partially attributed to the dilute acid cleanings performed. Wang, et al. found that only small quantities of foulants remained on the surface of CEMs following cleaning with a 1% HCl solution. Furthermore, the cleaning removed 97.5% of the calcium and 79.4% of the magnesium present on the CEM surface prior to cleaning. [51]

Nevertheless, IEMs in the present study were largely unimpaired and did not show fouling layers or the presence of major inorganic deposits. This is somewhat expected, as IEMs (especially Neosepta AMX and CMX) are known to be relatively robust compared to membranes used in traditional pressure-driven processes [46]. In pressure-driven membrane processes such as RO and NF, which reject the majority of both inorganic and organic constituents, compacted fouling layers and scaling are common [52, 53]. The findings in the present study point to ED as a valuable method to separate inorganic constituents from organic constituents in pretreated PW without substantial fouling on the IEM surface.

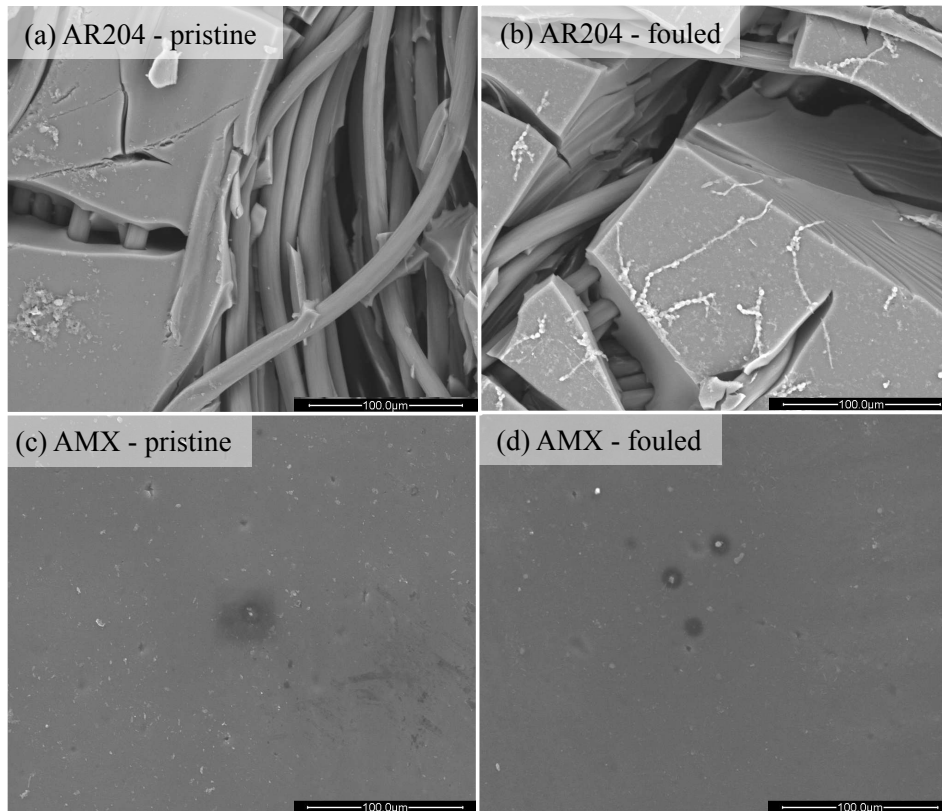


Figure 3.12 500X magnification for (a) pristine GE AR204, (b) fouled GE AR204, (c) pristine Neosepta AMX, and (d) fouled Neosepta AMX. The support layer of the GE IEMs cracked during desiccation but additional defects were not observed on either the fouled GE AR204 or Neosepta AMX. The fouled AMX appeared to be largely unimpaired.

3.3.2. Ion exchange capacity tests

Changes in IEM ion exchange capacity are summarized in Table 3.3. Ion exchange capacity is a fundamental physical property of IEMs that quantitatively demonstrates IEM changes in terms of number of counter ion equivalents per volume of membrane [12]. The ion exchange capacity of all IEM types decreased over the course of experiments. For the GE AR204 the ion exchange capacity decreased from 1.68 to 1.62 meq/g dry membrane and for the GE CR67 it decreased from 1.28 to 1.19 meq/g. For the Neosepta AMX the ion exchange capacity decreased from 1.55 to 1.36 meq/g and for the Neosepta CMX it decreased from 1.76 to 1.51 meq/g. While several ED studies have identified AEMs as more prone to fouling in the presence of organic matter than CEMs [12, 15, 17, 20], this was not the case in the present study. The GE IEMs were exposed to more foulants than the Neosepta IEMs over the course of 13 PW experiments, but

experienced a smaller decrease in ion exchange capacity. For both IEM types, CEMs were more impacted than AEMs.

Table 3.3 Ion exchange capacity results for pristine and fouled IEMs. Ion exchange capacity decreased for all IEMs, with CEMs being more affected than AEMs and the Neosepta IEMs more impacted than the GE IEMs

| IEM | Dry mass (g) | Dry thickness (mm) | IEC (meq/g) | % Difference from pristine IEM |
|-----------------------|-----------------|-----------------------|----------------|-----------------------------------|
| Pristine GE AR204 | 0.387 | 0.555 | 1.68 | - |
| Fouled GE AR204 | 0.415 | 0.543 | 1.62 | 3.7% |
| Pristine GE CR67 | 0.429 | 0.567 | 1.28 | - |
| Fouled GE CR67 | 0.440 | 0.540 | 1.19 | 7.2% |
| Pristine Neosepta AMX | 0.132 | 0.110 | 1.55 | - |
| Fouled Neosepta AMX | 0.123 | 0.103 | 1.36 | 12.7% |
| Pristine Neosepta CMX | 0.150 | 0.110 | 1.76 | - |
| Fouled Neosepta CMX | 0.150 | 0.123 | 1.51 | 14.5% |

CHAPTER 4

CONCLUSIONS

While ED is an established and mature desalination technology, the current literature lacks studies that analyze system performance for treatment of real PW using ED. Additionally, current research does not fully elucidate the transport of organic matter through IEMs. This thesis compared ASTOM Neosepta AMX/CMX and GE Water AR204/CR67 IEM performance and fouling during treatment of pretreated PW. It must be noted that there is inherent difficulty in conducting experiments with PW from the field due to the high variability of inorganic and organic components over time, which posed a variety of challenges embedded in the results of this study. IEM performance was measured for pristine and fouled IEMs as a function of current efficiency, ion removal, ion exchange capacity, and membrane stack resistance. Neosepta IEMs were more prone to fouling compared to GE IEMs, demonstrated by the increased stack resistance over the course of experiments with the Neosepta IEMs and minimal increases in stack resistance for the GE IEMs. However, the Neosepta IEMs outperformed the GE IEMs with higher current efficiency and a lower ratio of water to salt transfer during PW treatment. Furthermore, during integrity tests the Neosepta IEMs retained approximately 2% more volume of water in the diluate than the GE IEMs. Both types of IEMs appeared largely unimpaired and did not show fouling layers or the presence of major inorganic deposits when evaluated using ESEM.

There was a weak positive correlation ($R^2 = 0.6283$) between the percent TOC removed and the water mass transferred during experiments with the Neosepta IEMs, suggesting that the mechanism for TOC transfer using Neosepta IEMs is likely convection (i.e., TOC transfer with water). There was no correlation between TOC transport and water transport in experiments conducted with the GE IEMs, indicating that the mechanism for TOC transfer for the GE IEMs may be diffusion, confirming the results of previous ED studies. For PW treatment using both Neosepta and GE IEMs, there was some mass of TOC unaccounted for that was neither retained in the diluate nor transported into the concentrate. The mechanism proposed for this discrepancy is oxidation of TOC following diffusion into the electrode rinse and contact with the anode. Water from this study was used in a separate investigation to establish transport and fate of

organic matter in crops. Further work may include evaluation of organic contaminant degradation and oxidation during ED treatment.

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