ORGANIC FOULING IN MEMBRANE CAPACITIVE DEIONIZATION SYSTEMS

BY

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THESIS

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ABSTRACT

Membrane capacitive deionization (MCDI) is an emerging desalination technology that stores ions in the electrical double layer of porous electrodes. For most low-salinity water treatment technologies, fouling is a central issue, but few studies examine the its impact on MCDI. Fouling was evaluated using synthetic saline solutions with a combination of NaCl and $CaCl_2$ and the model organic foulant sodium alginate, known to complex with calcium, in a lab-scale MCDI system. Fouling caused an increase in the system pressure as well as 10-15% declines in salt adsorption and charge efficiency, and a similar increase in desalination energy over 20 hours of operation. The pressure increased overall, but showed cyclical increases and decreases suggesting that fouling was worsened with increased salt concentration during the discharge/brine generation. To evaluate the reversibility of fouling, pH adjustment, chelating agents, and hydraulic cleaning were applied to the membranes. Cleaning with pH adjustment reduced the system pressure, but still showed declines in system performance, even with cleaning cycles every 20 hours for 80 hours of operation. Over 80 hours, salt adsorption declined by up to 30% and energy use per ion removed increased by the same. The addition of EDTA to the basic cleaning solution reduced pressure and showed significant recovery of pre-fouling salt removal and energy use, indicating that the fouling could be reversible. After each cleaning cycle, adsorption, energy use, charge, and charge efficiency recovered to within 5% of their pre-fouling values, indicating that EDTA was well suited to break up the fouling layer created by the alginate and calcium.

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CHAPTER 1: INTRODUCTION

Worldwide, four billion people experience severe water scarcity for at least one month per year (Mekonnen and Hoekstra 2016). As populations increase in arid regions, non-traditional sources like reclaimed wastewater are increasingly relied upon to supplement decreasing freshwater reserves (Mekonnen and Hoekstra 2016). Reclaimed wastewater is an underutilized resource in the United States, where treated wastewater currently provides less than 5% of municipal yearly water use, but could provide 27%, more than 17 teraliters per year (Grant et al. 2012). As reclaimed wastewater becomes more essential, technologies to remove major contaminants remaining in wastewater effluent, mostly salts and organics, are crucial for ensuring safety in wastewater reuse (Hoek and Elimelech 2003; Haberkamp et al. 2007).

Wastewater is commonly treated with two stages of pressure-driven membrane filtration: first either micro- or ultrafiltration, then nanofiltration or reverse osmosis (Afonso, Jaber, and Mohsen 2004; Goosen et al. 2005). The process requires a high energy input (2-5 kWh/m^3) (Greenlee et al. 2009; K. P. Lee, Arnot, and Mattia 2011) and is susceptible to concentration polarization, the accumulation of solutes at the membrane surface, and membrane fouling, where contaminant molecules attach to the membrane and impede flux (Guo, Ngo, and Li 2012). Concentration polarization can enhance fouling (Hoek and Elimelech 2003), which necessitates energy and chemically intensive cleaning processes. It also increases system downtime and maintenance costs and reduces the lifetime of membranes (Zhang and Vecitis 2014). Water with a high organic content, like reclaimed wastewater, is especially prone to causing fouling (Ang et al. 2011).

In wastewater reuse, the interaction between dissolved solids and organics can cause significant problems for water treatment systems. Wastewater effluent tends to be high in organics, but exact concentrations vary significantly (Xu et al. 2008; A. V. R. Reddy et al. 2005). In many fouling experiments, alginate is a standard model for polysaccharide foulant molecules (Ang et al. 2011, 2011; H.-C. Kim and Dempsey 2013; S. Lee and Elimelech 2006). Polysaccharides, alginate included, complex with calcium ions through binding and cross-linking (figure 2) (K. Y. Lee and Mooney 2012; S. Lee and Elimelech 2006). The calcium ions serve as a bridge to connect alginate molecules in an "egg-box" formation that can create a thick gel layer on the membrane surface (H.-C. Kim and Dempsey 2013; S. Lee and Elimelech 2006). This layer accumulates in membrane filtration and electrodialysis in part due to the concentration polarization at the membrane surface (Vermaas et al. 2013; S. Lee and Elimelech 2006)

Typical membrane cleaning strategies include physical and chemical cleaning. Physical or hydraulic cleaning is increasing the flow rate to physically remove the foulant layer (Lin, Lee, and Huang 2010). Chemical cleaning can take several forms including pH adjustment and chemical additions. High pH cleaning (~pH 11) increases the solubility of alginate by deprotonating its carboxylic groups (Ang et al. 2011). Low pH cleaning (~pH 3), aims to completely protonate alginate's carboxylic groups, making it uncharged (Allison 1995). In many studies, the most effective cleaning strategy is the addition of chelating agent ethylenediaminetetraacetic acid (EDTA), which binds with metals (Ang, Lee, and Elimelech 2006; H.-C. Kim and Dempsey 2013). In a solution raised to pH 11, nearly all EDTA's functional groups are deprotonated (pKa: 2.72, 3.24, 6.68, and 11.12) and can bind with a divalent cation, giving it a high affinity for binding

with a complexed Ca^{2+} ion and making it much more effective at high pH (Li and Elimelech 2005).

Capacitive deionization (CDI) is a desalination technology that uses electrical charge to remove ions from water by polarizing porous carbon electrodes to reversibly store ions within the electrical double layer (R. Zhao, Porada, et al. 2013). An external power source applies a potential to two submerged electrodes, giving one side a positive charge and the other a negative charge. The negative and positive ions in the flow channel are each attracted to and adsorb to their respective electrode. The direction of current is then reversed, desorbing the ions into a brine solution and allowing partial recovery of the energy expended (Długołęcki and van der Wal 2013). Membrane capacitive deionization (MCDI) differs from CDI with the addition of ion exchange membranes (IEMs). An anion (cation) exchange membrane is positioned in front of the anode (cathode) (Figure 2), allowing only the desired ions into the electrode space. This addition minimizes co-ion repulsion into the flow channel during charging, enhancing salt removal (R. Zhao, Biesheuvel, and Wal 2012). Research indicates that MCDI can be less energy intensive than RO (Długołęcki and van der Wal 2013; R. Zhao, Porada, et al. 2013) at lower levels of influent salinity (L. Y. Lee et al. 2009). A central concept for understanding CDI and MCDI performance is charge efficiency, which compares the ions removed per unit of charge passed (Długołęcki and van der Wal 2013). Charge efficiency for CDI is typically near 60% and 80-95% for MCDI because of the ion exchange membranes (R. Zhao et al. 2010). The addition of organic foulants to CDI and MCDI has been studied minimally, but has been shown to lead to

declines in desalination performance for both (Mossad and Zou 2013; L. Y. Lee et al. 2009).

The objective of this study was to examine the impacts of organic fouling on the performance of a lab-scale MCDI reactor and to determine the reversibility of this fouling through hydraulic and chemical cleaning. Fouling was induced with model foulant sodium alginate and its complexation with calcium ions in the influent solution. Fouling was measured through changes in flow channel pressure and desalination performance metrics. The metrics to evaluate system performance include TDS removal, charge, charge efficiency, and energy consumption.

CHAPTER 2: LITERATURE REVIEW

2.1 Low-salinity water sources

As population and water demand increases, quantity and reliability of water sources in many areas are becoming insufficient (Mekonnen and Hoekstra 2016). To supply these areas with consistent water, non-traditional water sources are gaining importance (Greenlee et al. 2009). Seawater is an alternative source that has been utilized for many years with energy-intensive desalination processes (K. P. Lee, Arnot, and Mattia 2011). To avoid the high cost of seawater desalination, low-salinity sources like brackish groundwater and wastewater effluent are key resources to consider (Ghaffour, Missimer, and Amy 2013; Długołęcki and van der Wal 2013).

2.1.1 Brackish water

Brackish groundwater is a plentiful potential resource, particularly for inland areas with limited freshwater. It is also frequently a byproduct of natural gas extraction and processing that could be treated as a resource instead of waste requiring disposal (Xu et al. 2008). Brackish water, defined as 1,000-10,000 mg/L TDS, requires TDS removal to achieve drinking water standards, typically 500-1000 mg/L. Although it typically contains low levels of organic molecules (Greenlee et al. 2009), high levels of calcium, carbonate, sulfate, silica and boron, among others, can cause problems for membranes and other treatment systems due to increased concentration polarization and scaling (Greenlee et al. 2009; Tarquin, Fahy, and Balliew 2010). Brackish groundwater can vary significantly in different places, varying the level of treatment necessary and the issues associated with that treatment, but membrane fouling and

scaling remain central issues for filtration and electrodialysis (R. Zhao, Satpradit, et al. 2013; Greenlee et al. 2009).

2.1.2 Wastewater effluent

Wastewater is another important resource that is largely underutilized; it has the capacity to supply at least one third of the U.S. yearly municipal water demand (Grant et al. 2012). Wastewater reuse is complicated by the organic loading and dissolved solids in wastewater effluent (Ang et al. 2011). Dissolved solids, including sodium, calcium, and others, are typically present in wastewater effluent in low concentrations, but frequently exceed drinking water requirements, necessitating further treatment (Shon et al. 2006; Shon, Vigneswaran, and Snyder 2006). Wastewater typically receives at least primary and secondary treatment (Barker and Stuckey 1999). Primary treatment allows for settling of solids out of solution, and secondary treatment is a biological process that uses microorganisms to remove dissolved organic matter from the system (Gogate and Pandit 2004). The result of this process, secondary wastewater effluent, still contains organics, referred to as effluent organic matter (EfOM) (Jarusutthirak, Amy, and Croué 2002).EfOM is made up of natural organic matter (NOM) from surface waters and soluble microbial products (SMP) from secondary treatment processes, and its exact makeup can vary significantly (Shon, Vigneswaran, and Snyder 2006; H.-C. Kim and Dempsey 2013). EfOM can consist of a wide range of sugars, proteins and fats that can all contribute to problems for water reuse treatments like membrane fouling and pipe clogging (Shon, Vigneswaran, and Snyder 2006).

2.2 Low-salinity water treatment

Dissolved solids are typically removed through membrane filtration (Shon, Vigneswaran, and Snyder 2006) or electrodialysis (Goodman et al. 2013) to reach levels appropriate for water reuse (<500 mg/L for drinking water) (Tarquin, Fahy, and Balliew 2010). These ions can cause problems for reuse systems when they accumulate at a membrane surface or interact with organic molecules (Shon et al. 2006). A standard treatment for wastewater effluent reuse consists of an initial micro or ultrafiltration step followed by nanofiltration or reverse osmosis, removing both organics and dissolved solids (H.-C. Kim and Dempsey 2013; Hoek and Elimelech 2003). The major issues with all the membrane processes are fouling, mostly due to EfOM (H.-C. Kim and Dempsey 2013), and concentration polarization (Guha et al. 2015), which can enhance each other through cake-enhanced concentration polarization (Hoek and Elimelech 2003). The ultrafiltration pretreatment typically removes larger components of EfOM from the water, notably humic molecules (Imai et al. 2002), but does not remove many smaller organics, so the wastewater effluent organic makeup can still vary significantly after the pretreatment step (Shon et al. 2006). Kim and Dempsey (2008) reported total organic carbon of 17.8 mg/L in wastewater effluent, with at least 70% of TOC passing through a UF membrane. Imai et al. (2002) found dissolved organic carbon levels ranging from 3.5-31.6 mg/L at six different treatment plants and 2.3 mg/L at a treatment plant that included a UF post-treatment step. Ma, Allen, and Yin (2001) reported 14 mg/L TOC in wastewater effluent from one plant sample with no ultrafiltration.

After ultrafiltration, the water is treated further to remove additional dissolved solids and reach drinking water standards. This removal can be accomplished with several methods including reverse osmosis, nanofiltration, and electrodialysis (Ghaffour, Missimer, and Amy 2013). In reverse osmosis and nanofiltration, the pretreated water is pressurized and forced through another membrane, excluding dissolved solids as well as remaining organics (A. V. R. Reddy et al. 2005). The feed pressure for seawater is typically 6,000-8,000 kPa and for brackish water, 600-3000 kPa (Greenlee et al. 2009). In electrodialysis, the water flows through a stack of alternating anion and cation exchange membranes. An external voltage is applied to either side of the stack, attracting the anions and cations through the membranes, creating alternating channels of diluate and concentrate (Allison 1995). In practice, electrodialysis typically requires less pretreatment than RO to reduce fouling, but fouling is still expected after several months of operation (Korngold et al. 1970).

2.3 CDI/MCDI

Other desalination options that show promise for low-salinity water are emerging technologies capacitive deionization (CDI) and membrane capacitive deionization (MCDI) (R. Zhao, Satpradit, et al. 2013; R. Zhao, Porada, et al. 2013; Długołęcki and van der Wal 2013). CDI and MCDI remove ions from water with electrical charge and store them in the electrical double layers in the electrode pores. Two electrodes are charged by an external power supply and attract the anions and cations out of the bulk solution and into the electrode pores (Biesheuvel et al. 2011a). MCDI combines principles of CDI and EDR by using porous electrodes with ion exchange membranes. MCDI can achieve lower energy of removal per ion because of the introduction of ion

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exchange membranes next to the electrodes (R. Zhao, Satpradit, et al. 2013). The ion exchange membranes block co-ions in the electrode macropores from being expelled back into the flow channel (J.-H. Lee and Choi 2012). In CDI, this co-ion repulsion reduces charge efficiency because per unit of charge passed, the net ion removal from the flow channel is lower (Długołęcki and van der Wal 2013). The co-ions retained in the electrode pore space in MCDI also allow for higher counter-ion concentration in the macropores to achieve electroneutrality (R. Zhao, Porada, et al. 2013).

Both CDI and MCDI can be operated in constant current (CC) or constant voltage (CV) mode (figure 1). In CC mode, a set current is applied until a voltage limit is reached (typically 1-1.5 V), and the current is then reversed to remove the ions from the electrode (Biesheuvel et al. 2014). During this reversal, a portion of the energy applied can be recovered, with recoveries as high as 83% reported (Długołęcki and van der Wal 2013). This energy recovery can make the overall energy use of the system lower than other technologies like reverse osmosis under certain conditions (R. Zhao, Porada, et al. 2013), typically less than 5,000 mg/L TDS, making it a good option for low-salinity water desalination (R. Zhao, Satpradit, et al. 2013). However, as with membrane filtration and electrodialysis, fouling is an important consideration for operation.
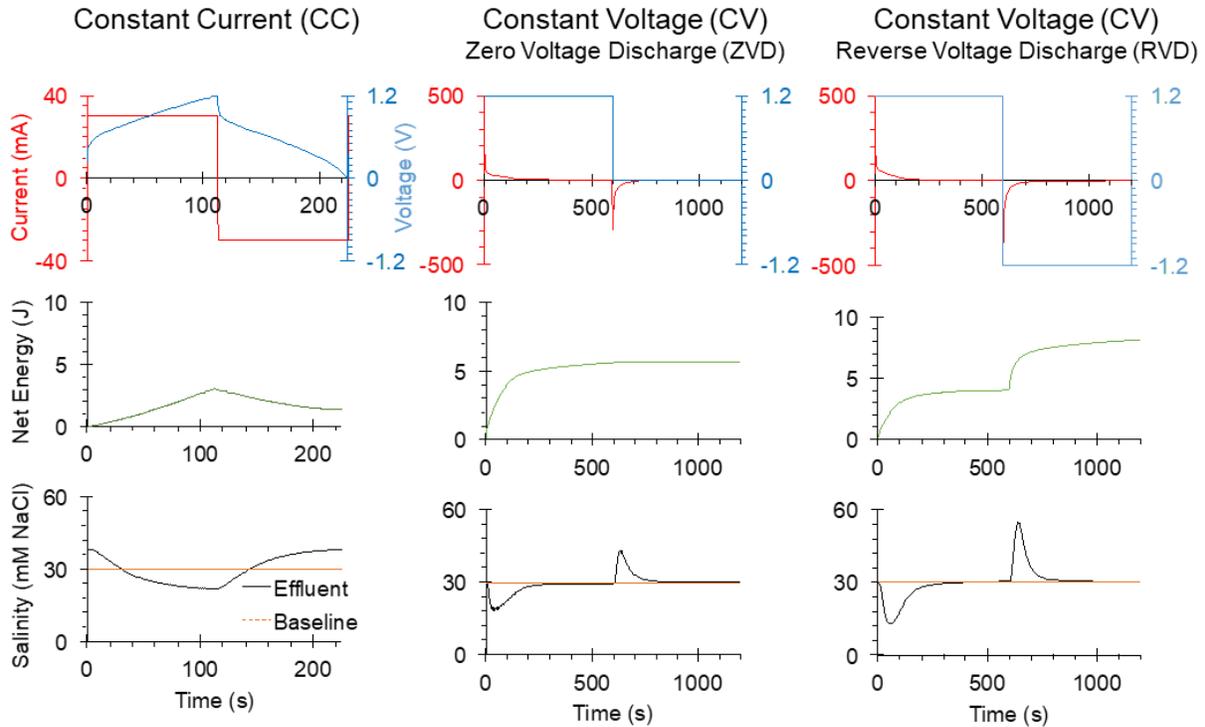
Figure 1: Current, voltage, energy and salinity plots for constant current and constant voltage (zero voltage discharge and reverse voltage discharge) for an MCDI system, showing energy recovery in CC and relative desalination performance between the three.

2.4 Cleaning cost

Membranes are a costly component of membrane filtration, electrodialysis and MCDI systems. Ion exchange membranes about 50% of the capital cost of an electrodialysis system (Grebenyuk et al. 1998). In practice, fouling prevention through chemical additives, membrane cleaning and eventual replacement can make up 40% of production costs in pressure-based filtration and 47% in electrodialysis (Greenlee et al. 2009; Grebenyuk et al. 1998; Ghaffour, Missimer, and Amy 2013). Chemical additives to prevent fouling and scaling can make up 12% of total water production costs (K. V. Reddy and Ghaffour 2007). The ultrafiltration pretreatment reduces fouling in reverse osmosis and nanofiltration by removing a portion of the organic content (A. V. R. Reddy

et al. 2005). The combination of high organic content and dissolved solids can work together to increase fouling in both reverse osmosis and electrodialysis (Guha et al. 2015; Korngold et al. 1970). The influence of inorganic scaling on one membrane can exacerbate organic fouling on the other membrane in electrodialysis, so effective pretreatment can significantly reduce the interactions between the two and reduce fouling (Korngold et al. 1970).

2.5 Membrane filtration fouling

Pressure-based membrane filtration technologies are particularly vulnerable to organic fouling due to concentration polarization at the membrane surface (Hoek and Elimelech 2003). Reverse osmosis, micro-, ultra-, and nanofiltration all utilize pressure to separate water from solutes through a membrane (Amy 2008). The solutes that cannot permeate through the membrane accumulate at the surface, causing a concentration increase approaching the membrane, concentration polarization (Hoek and Elimelech 2003). When organics are added to this system, they can accumulate and attach to the membrane, creating a fouling layer that impedes water flux, increasing required pressure and decreasing permeate production (S. Lee and Elimelech 2006). Organics typically seen in wastewater effluent, polysaccharides, humics, and proteins, can all contribute to this fouling (H.-C. Kim and Dempsey 2013; Ang et al. 2011), but polysaccharides can form a complex with calcium ions, resulting in a gel layer that can significantly increase fouling (Ang, Lee, and Elimelech 2006). The gel or cake layer that builds up on the membrane surface increases the concentration polarization effect (cake enhanced concentration polarization), increasing fouling (Hoek, Bhattacharjee, and Elimelech 2003). An additional force, diffusiophoresis, has been shown to enhance

this effect even further through the electric field created by differences in the diffusivities of anions and cations in low-salinity water (Guha et al. 2015). All of these forces combined can create a positive feedback loop that can enhance and accelerate the fouling process significantly (Guha et al. 2015), necessitating frequent cleaning and membrane replacement.

2.6 Electrodialysis fouling

ED fouling can reduce ion removal and increase energy use, and is of particular concern for water with high organic loading and salt content (Allison 1995; Korngold et al. 1970). ED fouling research focuses on AEM fouling due to the negative charge on most organic foulants attracting them to the AEM (Allison 1995; Bazinet and Araya-Farias 2005). The negative charge leads to accumulation at the AEM surface (H.-J. Lee et al. 2002) and adsorption into the AEM pores (H.-J. Lee et al. 2009). These organics are typically larger molecules (H.-J. Lee et al. 2002) and enter the membrane pores and adhere, reducing selectivity (Grebenyuk et al. 1998) and increasing resistance (James Watkins and Pfromm 1999). The selectivity of the membrane can decrease because the negatively-charged organic molecules stick in the positively-charged pores, allowing cations to pass through (Vermaas et al. 2013). The accumulation at the surface of the membrane is a phenomenon similar to concentration polarization in membrane filtration systems (Vermaas et al. 2013). However, in ED/EDR, this accumulation is due to electrical attraction of the foulants to the membrane. As the accumulation of foulant at the surface increases, the layer thickens and compacts, increasing resistance at the membrane surface and obstructing ion flux (H.-J. Lee, Moon, and Tsai 2002).

Surface accumulation due to negative charge contributes to fouling, but adsorption into the membrane is another aspect. H.-J. Lee et al. (2009) applied Freundlich and Langmuir isotherms to adsorption of three organic foulants and found that the adsorption capacity of a foulant correlated with its potential for irreversible fouling. Although the foulants had similar surface charges, foulants with higher adsorption capacity led to more significant irreversible fouling. H.-J. Lee et al. (2009) differentiate between foulants too large to penetrate the membrane and accumulate at the surface and those small enough to penetrate the membrane pores, but notes that both can lead to significant increase in resistance.

Studies examining CEM fouling in ED look mainly at mineral scaling (Cifuentes-Araya, Pourcelly, and Bazinet 2011). Influent water with high levels of calcium, magnesium and carbonate, like many brackish groundwaters, are typically affected by this type of fouling (Greenlee et al. 2009). The buildup of inorganic molecules at the surface can lead to decreased surface charge and increased resistance, reducing the ED performance by (Bazinet and Araya-Farias 2005).

2.7 CDI/MCDI fouling

CDI and MCDI fouling studies saw declines in desalination performance with the introduction of organic foulants and recovery through cleaning, but minimal research exists on these topics (Mossad and Zou 2013; L. Y. Lee et al. 2009). Mossad and Zou (2013) examined the impact of humic acids on CDI operation, finding declines in performance over 30-hour operation periods. They attribute these declines to humic molecules blocking electrode pores and saw recovery with alkaline cleaning. They observed similar declines and recovery with the addition of multivalent cations, including

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calcium, suggesting minimal interaction or complexation between the organics and cations.

Lee et al. (2009) examines MCDI for RO reject water from secondary wastewater effluent with various pretreatments. They observed fouling leading to extreme pressure increase stopping the experiments at the unadjusted pH of 7.7 and minimal fouling with pH adjusted to 6.5. They attributed the lessened fouling to the higher Cl^- concentration causing accumulation and preferential adsorption of Cl^- ions at the AEM, protecting the membrane from negatively charged organics and reducing organic adsorption into the membrane. Additionally, they noted that carboxylic groups in the organic molecules would be more protonated at lower pH, reducing their negativity and attraction to the AEM. Similar effects have been observed in ED systems at low pH (D. H. Kim, Moon, and Cho 2003; H.-J. Lee, Moon, and Tsai 2002).

As low-salinity water sources become more widely utilized, lowering the treatment cost is crucial. The impact of organics on these systems is a key factor in determining lifetime, pretreatment and replacement costs (Ghaffour, Missimer, and Amy 2013). Organic fouling can significantly impact membrane filtration and electrodialysis systems, so more research on its impact on MCDI is necessary to gain a better understanding of the feasibility of implementing the technology.

CHAPTER 3: MATERIALS AND METHODS

3.1 Reactor design

The MCDI reactor consisted of two graphite current collectors, each containing a carbon electrode, held in place by two acrylic frames (Figure 2). The flow channel had a width of 300 micrometers and an area of 20 cm^2, supported by two plastic mesh spacers (150 μm thick, Cole-Parmer, Vernon Hills, IL) and enclosed by a gasket (500 μm thick, AAA-Acme Rubber, Tempe, AZ). The flow channel was bordered by two IEMs (Type A, Fujifilm, Tilburg, Netherlands), with the anion exchange membrane in front of the anode and the cation exchange membrane in front of the cathode. Each membrane's effective surface area was also 20 cm^2.
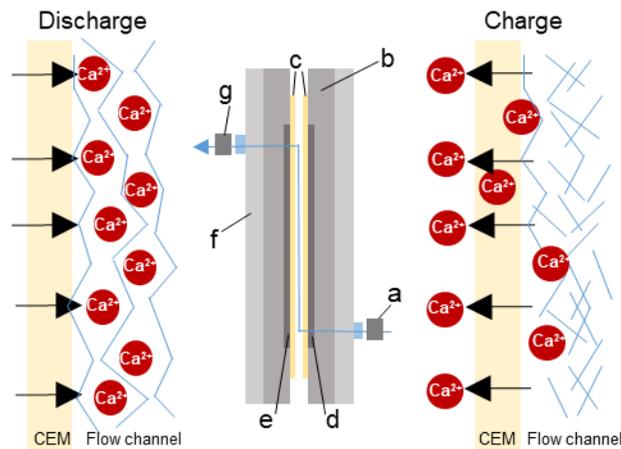

Figure 2: Diagram of the alginate/calcium complex formation during discharge and breakup during charge, and a diagram of the reactor showing (a) pressure sensor, (b) graphite current collector, (c) ion exchange membranes, (d) working electrode, (e) counter electrode, (f) reactor frame, and (g) conductivity probe.

3.2 Electrode fabrication

The electrodes were made of powdered activated carbon (Sigma-Aldrich, St. Louis, MO) and binder polyvinylidene fluoride (PVDF, Alfa Aesar, Ward Hill, MA). The

PVDF was initially dissolved in dimethylacetamide (DMac, Sigma-Aldrich, St. Louis, MO), at a concentration of 60 mL of DMac per gram PVDF, by stirring on a hot plate at 70°C for at least 12 hours. Activated carbon was added in a ratio of 9:1 (activated carbon:PVDF) and stirred for 12 hours. An aliquot of the slurry (4 mL) was pipetted into the 20 cm^2 by 1 mm deep groove in the graphite plate. The groove was overfilled to allow for solvent evaporation. The electrodes were dried by placing the graphite plates onto a hot plate at 70°C for one hour, until the electrodes appeared dry. The electrodes were then submerged in 30 mM NaCl (VWR International, West Chester, PA) for 12 hours.

3.3 Experimental setup

The MCDI cell voltage was controlled with a potentiostat (model VSP, Bio-Logic USA, Knoxville, TN) channel with a current booster (model VSP/4A-01, Bio-Logic USA, Knoxville, TN). Cell voltage was alternated between 15 minute periods of 1 V during desalination and -1 V during brine generation. Saline influent was pumped through the reactor at a rate of 1 mL min^{-1} with a peristaltic pump (Model 77201-60, Masterflex, Vernon Hills, IL). The flow channel pressure was measured on the influent side by a pressure sensor (Model P51, SSI Technologies, Janesville, WI). The effluent conductivity was measured by a conductivity probe (ET908, eDAQ, NSW, Australia) with a 93 μL flow cell (Figure 2).

Each experiment started with at least three 40-cycle charge-discharge experiments to establish a performance baseline. Afterward, the 25 mg/L of sodium alginate (from here) was added to the influent solution for another 40-cycle charge-discharge experiment. A 30-minute cleaning cycle was then conducted with one of three

cleaning solutions recirculated from a reservoir at 4 mL min^{-1}. After cleaning, the system

operated in charge-discharge mode with no foulant for 2-3 hours to remove residual

cleaning solution. After this period, another 40-cycle fouling experiment was conducted.

This was repeated 3 times to reach a total of 4 fouling cycles for a desired electrolyte

concentration and cleaning method. The cleaning methods evaluated were high pH, low

pH and EDTA at high pH. The high and low pH solutions were deionized water adjusted

to pH 11 or pH 3 with 0.1 M NaOH (Fisher Scientific, Hampton, NH) or HCl (Sigma-

Aldrich, St. Louis, MO). The chelating solution was the same as the pH 11 solution, but

also included 1 mM EDTA (Sigma-Aldrich, St. Louis, MO).

With an influent concentration of 30 mM NaCl, pressure remained constant at

around 0.4 psi with and without 25 mg/L of sodium alginate (Sigma-Aldrich, St. Louis,

MO). To induce fouling, the calcium concentration was incrementally increased in the

saline test while keeping conductivity constant. 28 mM NaCl + 1 mM CaCl$_2$ (Sigma-

Aldrich, St. Louis, MO) and 25 mM NaCl + 2.5 mM CaCl$_2$ also remained constant at 0.4

psi with and without 25 mg/L sodium alginate. At 20 mM NaCl + 5 mM CaCl$_2$, the

pressure started to increase within the first cycle, and this concentration was used for

the rest of the fouling experiments. The levels of organics, calcium and sodium chloride

in the influent are on the high end of concentration ranges in wastewater effluent (Shon

et al. 2004b, 2004a, 2006; Haberkamp et al. 2007; H.-C. Kim and Dempsey 2008).

Wastewater effluent also contains other ions including sulfate, phosphate, iron, and

manganese (Madaeni and Samieirad 2010; Mohammadi, Madaeni, and Moghadam

2003), but the influent solution was simplified to examine the calcium-polysaccharide

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cross-linking, a major contributor to fouling in other desalination systems (Y. Zhao, Song, and Ong 2010; S. Lee and Elimelech 2006).

3.4 Performance metrics

The central performance metrics examined were charge efficiency, adsorption, and energy consumption. The total adsorption is calculated by conversion of effluent electrical conductivity (EC) to mg/L TDS through the equation (Rhoades 1996)

$$TDS = EC * 640$$

The amount of TDS removed from the effluent by adsorption, S_{ads}, is calculated by the equation

$$S_{ads} = \int (S_{base} - S_{eff}) * Q * dt$$

where S_{base} is the baseline salinity, S_{eff} is the effluent salinity, Q is the flow rate and t is the time. Because our solution is made up of mono- and divalent ions, we analyzed the effluent of 3 charging and 3 discharging stages, with and without alginate, with ICP (Optima 8300, PerkinElmer, Waltham, MA) to determine the Ca^{2+}:Na^+ ratio. We found the ratio to be the same as the influent, so we used a constant ratio to determine the total charge of ions removed. The total charge, C, is calculated by the equation

$$C = \int I * dt$$

where I is the current and t is time. The charge efficiency, Λ, is a measure of the ions removed per total charge passed. It is calculated by the equation

$$\Lambda = \frac{S_{ads}}{C} * F$$

where F is Faraday's constant. (R. Zhao, Biesheuvel, and Wal 2012). Additionally, the energy, E, is reported in joules per mg TDS removed. This is calculated by the equation

$$E = \frac{C * V}{S_{ads}}$$

where V is the voltage.

3.5 Membrane characterization

After each series of fouling and cleaning experiments, the IEMs were removed from the reactor and replaced for the next experiment. The fouled membranes were characterized to determine their permselectivity. Permselectivity was evaluated using a two-chamber flow cell (chamber dimensions: 2 cm x 5 cm x 5 cm), with chambers separated by the membrane to be tested. The chambers were filled with 500 mM and 100 mM NaCl, which flowed through the chamber at 5 mL*min⁻¹ while the chamber was stirred vigorously with a stir bar. A reference electrode was placed in each chamber and the voltage between the two was measured every second for 15-45 minutes.

The average measured voltage, E_m, is used with the following equation to calculate permselectivity, α:

$$\alpha = \frac{\left[\left[E_m / (\frac{RT}{F} * \ln \frac{a^H}{a^L}) \right] + 1 - 2t_M^S) \right]}{2t_X^S}$$

where R is the gas constant, T is absolute temperature, a^H and a^L are the activity of the solutions on the high and low side of the membrane, and t^s_M and t^s_X are the transport numbers of the co- and counter-ions (M. Geise et al. 2014).

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Pressure fluctuations

The flow channel pressure increased throughout the fouling experiment. Influent pressure fluctuated with each MCDI charge cycle, increasing when charge was injected into the cell and decreasing during the discharge. The fluctuation magnitude increased with cycle number, representing up to one third of the local average pressure value (Figure 3). This fluctuation reflects the increase and decrease in flow channel ion concentration during the charge and discharge cycles, implying a link between pressure and salt concentration. The ionic concentration increased in the flow channel during cell discharge because the ions desorb from the electrode and are expelled through the IEMs, increasing from 0-80 mg/L TDS during the charging stage to over 4000 mg/L at the beginning of the discharge. The higher salt concentration in the flow channel led to Ca^{2+}-alginate complexation and accumulation as a foulant layer, creating a flow restriction and measurable pressure increase. The pressure reduction during the charging stage suggests the partial breakup of the foulant layer when the ion concentration decreases, but the overall pressure increase over 40 cycles indicates that some foulant remained during both charge and discharge. As the average pressure increased over time, the minimum and maximum salt concentration in the effluent decreased in magnitude, as shown in Figure 3 A and B. The increase in peak concentration during charge and decrease during discharge suggest that the foulant layer is accepting ions during discharge and releasing ions during charge, reducing the magnitude of the concentration maximum and minimum.
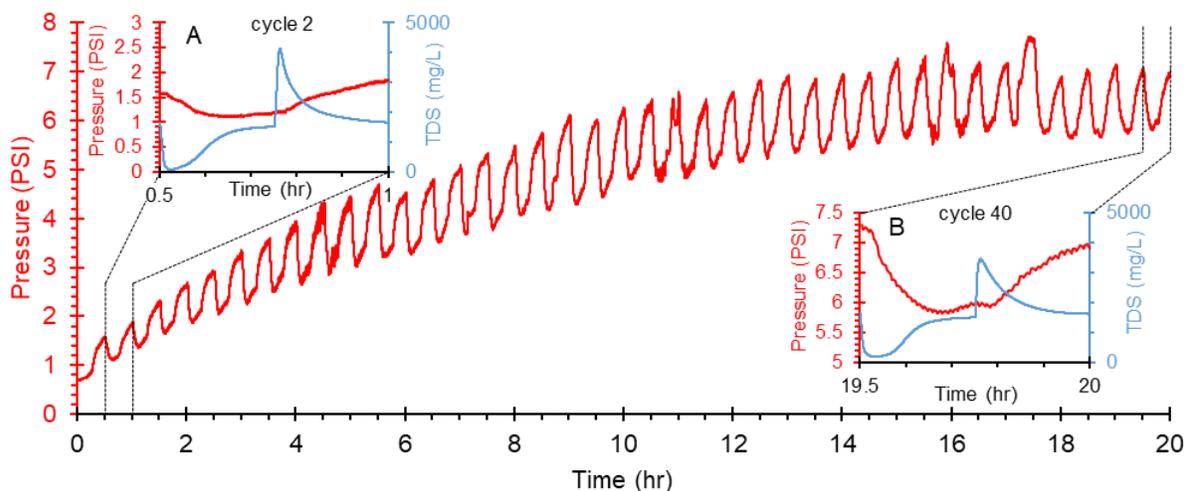
Figure 3: Pressure profile during a 20-hour fouling experiment, showing overall pressure increase throughout the experiment, with local increases during the discharge cycle and decreases during charge cycle.

4.1.1 Pressure recovery from cleaning

All three cleaning cycles initially lowered the flow channel pressure significantly (Figure 4). The average starting pressure of each fouling cycle increased by less than 100% over the four cycles, apart from the final acidic cycle. Although the average starting pressure was similar for all cleaning types, the pressure profile during cleaning varied. Cleaning the flow channel with base reduced pressure slowly and consistently over time, stabilizing at a higher final pressure with each cleaning. Acidic cleaning caused a quick initial drop in pressure, then stabilized for the remainder of the 30-minute cycle. Acidic cleaning also stabilized at a higher pressure with each cycle. The EDTA/base cleaning also caused a quick initial pressure drop, followed by stabilization. This cleaning method appeared to level off at a similar pressure with each cycle, unlike the previous two methods. Despite the pressure recovery with each cleaning method, the recovery of adsorption, charge, charge efficiency, and energy consumption differed
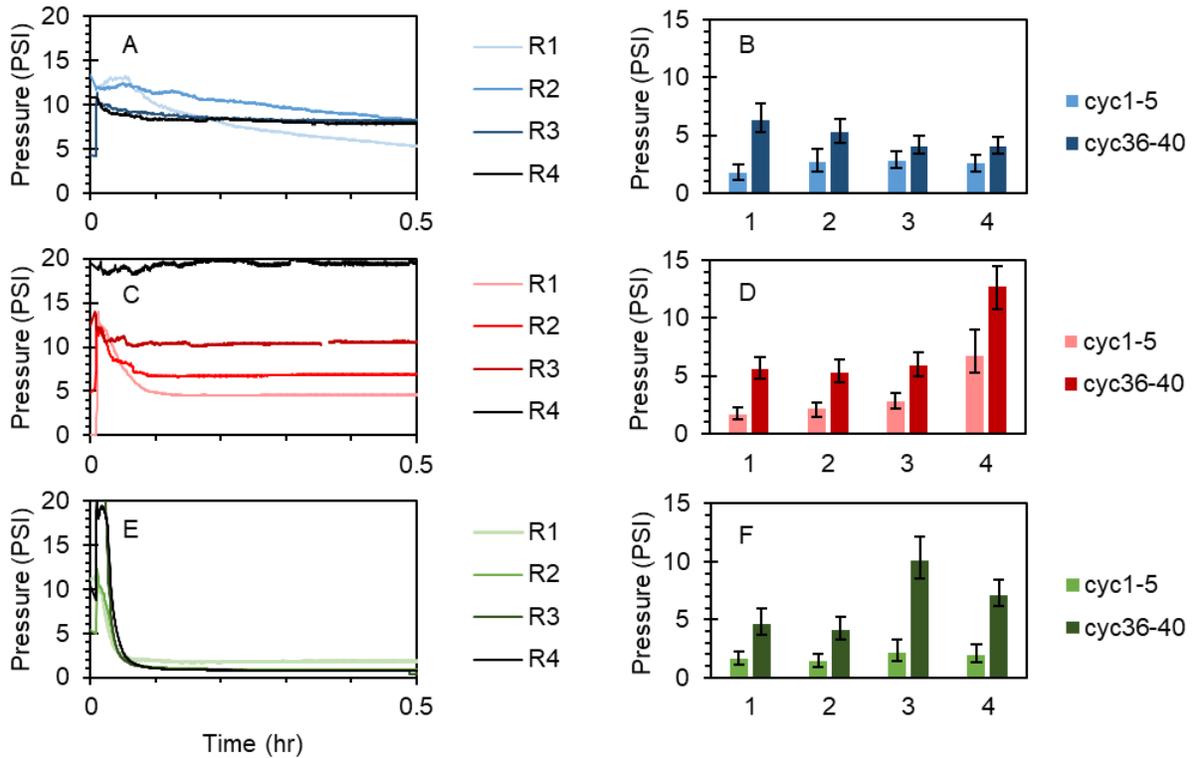
greatly between the three.

Figure 4: Pressure profiles of the four cleaning cycles and operational starting and ending pressures during fouling showing (A) and (B) basic cleaning, (C) and (D) acid cleaning and (E) and (F) basic cleaning with EDTA.

4.2 Impacts of fouling on desalination performance

Organic fouling caused significant declines in MCDI performance. For the 0, 1 and 2.5 mM Ca^{2+} influent experiments, system parameters remained stable with and without alginate present. Adsorption averaged .49 mg/cycle, charge efficiency at 80%, and energy consumption averaged 4.1 J/mg removed. This is higher than typical RO energy of removal (Greenlee et al. 2009; K. P. Lee, Arnot, and Mattia 2011) and than the pre-fouling energy used in Lee and Elimelech (2006), 3.6 J/mg, but this is expected because the MCDI system is operating in reverse voltage discharge mode which maximizes adsorption does not optimize energy use (Biesheuvel et al. 2011b). Energy

consumption increased as charge efficiency declined by 6-10% over 40 cycles (pre-

cleaning). The adsorption per cycle declined by 10-16% over the 40-cycle experiment,

and the charge passed during desalination declined by 4-9%. In RO research, permeate

flux can decline by up to 75% under influent conditions with lower salt content and

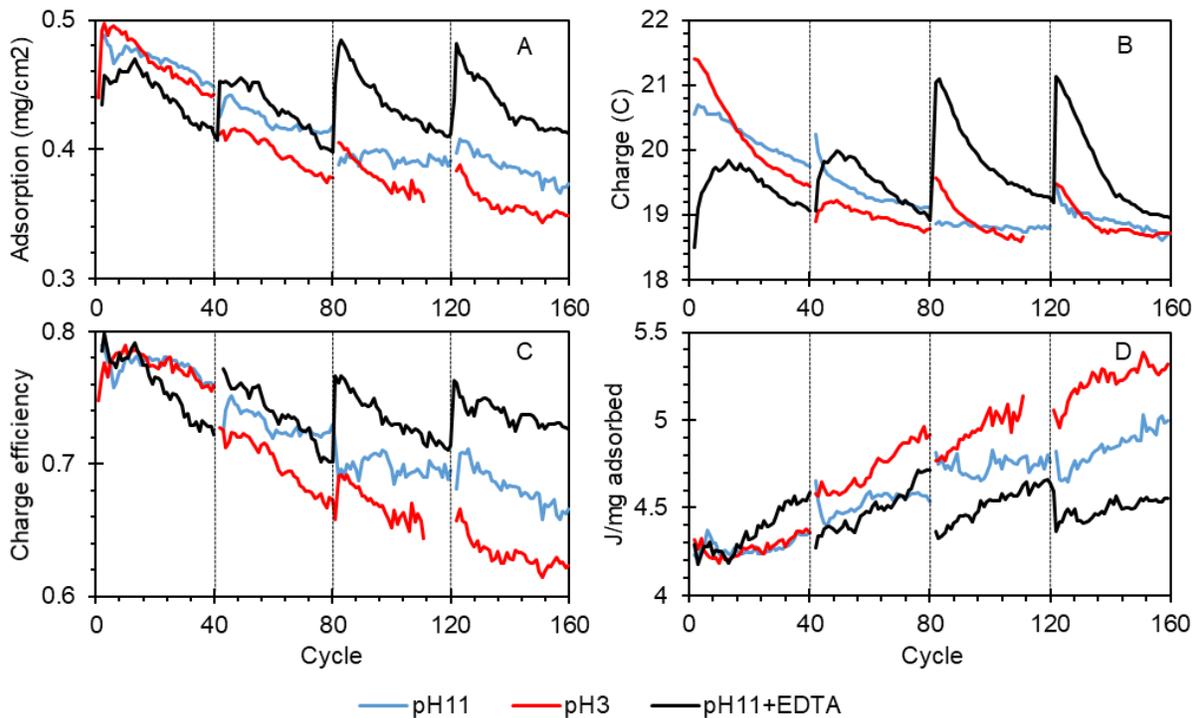organic loading than used here (S. Lee and Elimelech 2006; S. Lee, Ang, and Elimelech

2006)

Figure 5: (a) Adsorption in mg of TDS per cm^2 of membrane area decreases during the fouling cycles. The dashed lines represent pauses in the experiment for cleaning. (b) Total charge per cycle (c) Charge efficiency over 160 charge-discharge cycles. (d) The energy per mg of TDS removed.

Since the foulant layer contained Ca^{2+} ions ionically bonded to alginate

molecules, it could serve as a source or sink for calcium ions during the charge or

discharge stage, reducing flux out of or into the flow channel. The decline in charge

reflects an increase in resistance, but the greater decline in adsorption indicates the foulant layer interfered with ion flux within the flow channel and through the IEMs. The interference is likely because of the foulant layer's ability to accept and release ions into the flow channel or through the IEM, acting as an ion source or sink. There was no change in the permselectivity of the IEMs after fouling, so the foulant layer did not affect the IEM's ability to reject co-ions. The energy consumption with alginate increased by 6-12% over 40 cycles, partly due to the decrease in charge efficiency from the foulant layer's interference with ion flux.

4.2.1 Foulant removal through pH adjustment and chelation

Although all cleaning methods indicated some foulant removal through pressure recovery, the performance parameters illustrate clear differences in the impacts of the cleaning methods. For the acidic cleaning, the charge efficiency declined by 22%, adsorption decreased by 29%, and energy consumption increased by 30% over 160 cycles with periodic cleaning (Figure 5). As shown in figure 5, the intermittent cleaning cycles did not lead to recovery of the parameters; their trend is consistent despite the four cleaning cycles.

For basic cleaning, the charge efficiency decreased by 17%, adsorption declined by 22%, and energy increased by 23% over the four fouling and cleaning experiments. As shown in figure 5, the decline/increase in parameters appears consistent throughout, with no major shifts after cleaning cycles. This suggests that the pH adjustment dissolved or removed foulant buildup in the flow channel, reducing pressure, but did not effectively clean the membranes. This is consistent with Ang, Lee and Elimelech (2006),

who found that basic cleaning was only slightly more effective for calcium-alginate fouling than hydraulic cleaning with DI water.

Organic fouling was reversible when the flow channel was cleaned with a basic chelating solution. Adsorption, charge, charge efficiency and energy consumption all showed recovery to within a 10% difference from their pre-fouling baseline values for each cleaning cycle. At pH 11, all of EDTA's carboxylic groups are deprotonated, increasing its ability to bond with calcium (Li and Elimelech 2005). In figure 4, we see that the pressure decreases rapidly during cleaning cycles and continues in successive fouling/cleaning cycles. With EDTA, the pressure drop is also reflected in the other system parameters. By the end of 160 cycles, the adsorption had decreased by 16% and charge efficiency by 9%, showing much less decline in system performance compared to the other cleaning methods. EDTA cleaning was also an effective cleaning method in several RO alginate/calcium cleaning papers, leading to nearly 100% flux recoveries in some cases (Ang, Lee, and Elimelech 2006, 206; Ang et al. 2011), indicating that it is a good option for removing alginate/calcium complexing. The recovery of the adsorption, charge efficiency and energy consumption indicates that the foulant layer on the membranes is removed. This is likely due to EDTA attracting the Ca^{2+} ions out of the alginate complex, removing an important component of the fouling layer and allowing easier removal of the foulant.

CHAPTER 5: CONCLUSION

The addition of organic foulants to MCDI influent solutions led to declines in system performance that are reversible in the presence of a chelating agent. Using a model foulant alginate and a mixture of NaCl and $CaCl_2$, we induced fouling in the system and observed a decline in the central performance metric, charge efficiency, likely due to a foulant layer serving as an ion source and sink. Flow path pressure increased and decreased with the flux of ions into and out of the foulant layer building up in the flow channel. The importance of calcium cross-linking in the foulant layer led to fouling being highly reversible with EDTA, which binds to divalent cations like Ca^{2+}. The reversibility is promising for future research and implementation of MCDI for brackish water and wastewater reuse. Further research on additional foulant types like proteins, humics, and lipids will augment our understanding of MCDI's feasibility for wastewater effluent reuse. Further work using effluent organic matter instead of model foulants will also aid in the understanding of MCDI as a tool for wastewater reuse.

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