

FOULING CONTROL IN ELECTRODIALYSIS FOR WASTEWATER
APPLICATIONS

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By :

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Abstract

Nutrient removal is one of the primary goals of wastewater treatment and large amounts of ammonia are present throughout the wastewater treatment process. Conventional ammonia removal technologies are energy intensive and do not result in recoverable forms of the nutrient. Anaerobic dewatering side-streams are the liquid recovered during the biosolids dewatering processes following anaerobic digestion. The dewatering side-streams contain high concentrations of ammonia (~1000 mg/L $\text{NH}_4\text{-N}$) making them an excellent candidate for resource recovery technologies. In this study electro dialysis (ED) was investigated for ammonia ($\text{NH}_4\text{-N}$) recovery from anaerobic dewatering side-streams with an emphasis on fouling and scaling control on ion exchange membranes (IEMs).

The experimental set-up consisted of 3 bench-scale electro dialyzers operating in parallel. The dewatering side-stream (centrate) was collected directly from centrifuges at a local WWTP and pretreated using a 0.3-mm screen. Electro dialyzer operation over 2.25 hrs achieved 95% $\text{NH}_4\text{-N}$ removal and the ammonia separation rate was slowed down by the concentration gradient between concentrate and diluate streams. A combined 269 hrs of operation during fouling experiments showed that electro dialysis (ED) performance decreased over time due to IEM fouling and thus clean-in-place (CIP) procedures was conducted every 60-120 hrs to restore the ED effectiveness. The two stage CIP procedures consisted of a NaCl Clean (5% NaCl, 2 hrs recirculation) and an Acid Clean (5% v/v HCl, 2 hrs recirculation). The NaCl Clean targeted organic fouling and the Acid Clean removed scales that precipitated on the IEMs. CIP procedures were able to recover 84-90% of the

initial separation efficiency, the permanent loss in separation efficiency indicating that a portion of IEM fouling (10-16%) is irreversible. The higher applied voltage condition (7.5 V) showed faster fouling rates compared to low voltage conditions (4.5 V), while the degree of irreversible fouling was independent of the applied voltage. Organic fouling and inorganic scaling were individually quantified during CIP procedures using electrochemical impedance spectroscopy (EIS). While both fouling and scaling contributed significantly to the overall increase in the IEM stack resistance (63% scale formation, 37% organic fouling), inorganic scaling was found to play a more important role in reducing the separation rate in ED. ICP and SEM-EDS analysis identified the scale that formed on the surface of the IEMs as mostly of CaCO_3 precipitation with smaller amounts of struvite. This finding indicates that the pretreatment of dewatering side-streams should be more focused on removing divalent cations (Ca^{2+} and Mg^{2+}), but also still consider organic foulant removal for its treatment in ED. Since organic fouling primarily affects anion exchange membranes (AEMs), the impacts of fouling were investigated on two types of AEMs (AR908, AR204). Fouling experimentation showed minor differences in current density and separation efficiency over 269 hrs of operation, with AR204 AEMs showing signs of worse irreversible fouling. Particle size analysis of centrate suggested that large suspended particles could obstruct electro dialyzer chambers. Screening pretreatment (0.3 mm) effectively removed large particles and mitigated clogging issues without having to increase intermembrane distances.

The experimental results suggest that ED is a promising technology for recovering ammonia from nutrient rich wastewaters. ED was able to efficiently achieve high levels of

ammonia separation from centrate, while fouling was shown to be manageable using CIPs at reasonable intervals. Overall ED was shown to be an effective way to recover ammonia from dewatering side-streams, but pretreatments targeting scaling and organic fouling could better mitigate performance losses due to fouling and further improve the process.

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List of Abbreviations

WWTP	Wastewater treatment plant
BNR	Biological nutrient removal
ANNAMOX	Anaerobic ammonia oxidation
MABR	Membrane aerated biofilm reactor
IEM	Ion exchange membrane
ED	Electrodialysis
CEM	Cation exchange membrane
AEM	Anion Exchange Membrane
EDR	Electrodialysis Reversal
CIP	Clean-in-Place
sCOD	Soluble chemical oxygen demand (mg-COD/L)
TSS	Total suspended solids (mg-TSS/L)

1. Introduction

Wastewater treatment engineering is a very mature industry and modern wastewater treatment plants (WWTP) are able to reliably reach regulatory limits producing low to zero impact effluent (Foley et al., 2010). Since regulatory limits are no longer the limiting factor, within the industry a paradigm shift is taking place with a new focus on reducing energy input requirements and looking at wastewater as a resource with valuable products to be recovered. With this change in motivation there is serious interest in reevaluating how nutrients are managed at all stages of the treatment process and in looking for recovery opportunities (Batstone et al., 2015).

The two primary nutrients in wastewater are phosphorus and nitrogen, both are strictly regulated by governing bodies in treatment plant effluent. Throughout the wastewater treatment process nitrogen content in wastewater can take several different forms. The forms are split into particulate and soluble forms and include organic nitrogen, free ammonia (NH_3), ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-) (Eddy et al., 2014). Ammonia is required to be removed in wastewater treatment process due to ecosystem toxicity, effects on discharge area dissolved oxygen, mitigation of eutrophication and controlling nitrogen concentrations for reuse applications (Eddy et al., 2014). While possibly harmful to the environment if the nutrients are not properly managed, there are serious advantages to using processes that allow for recovery from wastewater. Recovered nutrients that are key for agricultural growth and can be converted into commercial fertilizers creating a revenue stream from waste treatment while reducing the demand from non-renewable sources such as mineral deposits (Mehta et al., 2015).

There are currently several conventional nitrogen removal processes used in wastewater treatment plants and some promising emerging technologies. Treatment plants generally rely on biological nutrient removal (BNR) within a conventional activated sludge system which requires significant energy inputs in the form of aeration contributing upwards of 50% of overall treatment costs (Foley et al., 2010). The other downsides to conventional BNR for nitrogen removal are slow growth rate of nitrifying bacteria which demands long retention times, the conversion of nitrogen into an unrecoverable form, and the sensitivity of the microorganisms to changes in sludge characteristics such as dissolved oxygen, pH and temperature (Eddy et al., 2014). Emerging technologies such as anaerobic ammonia oxidation (ANAMOX) and membrane aerated biofilm reactors (MABR) are promising developments relating to energy and footprint requirements, but do not result in recoverable forms of the nutrient (Batstone et al., 2015).

Ion exchange membranes (IEM) are able to selectively separate ions from complex solutions given a sufficient driving force. This makes IEM processes such as electrodialysis (ED) well suited for waste stream nutrient recovery as phosphate and ammonia are both in their charged forms at typical wastewater pH ranges (Eddy et al., 2014). ED is a proven technology with broad range of applications in desalination, food and beverage industry, and chemical processing (Strathmann, 2010). ED is an electrochemical process that utilizes alternating layers of IEMs to separate charged components of a solution into a single concentrated stream using a potential difference as the driving force. The concentrated nutrient streams produced by ED can be then be used as a liquid fertilizer or go through further refining to produce a more versatile product. The use of electrodialysis to separate

nutrients from wastewater is an emerging application of the technology with a lot of opportunity for innovative applications in the wastewater treatment industry.

1.1 Literature Review: ion exchange membranes and electrodialysis

Ion exchange membranes are the membrane form of ion exchange resin and consist of a polymer matrix backbone with charged groups fixed throughout. The two categories of IEMs are cation-exchange membranes (CEM) and anion-exchange membranes (AEM). CEMs contain fixed negative groups while AEMs have positive groups which give the membranes their exclusion properties (Strathmann, 2010). There are a wide variety of charged groups that can be used in IEMs but the most common are $-\text{NH}_3^+$, NRH_2^+ , NR_2H^+ and NR_3^+ for AEMs and $-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{PO}_3^{2-}$ and $-\text{PO}_3\text{H}^-$ for CEMs (Hassanvand et al., 2017). Charged ions with the opposite charge of the bound groups are known as the counter ions and are able to pass through freely as they balance out the fixed charges of the membrane. Ions with an identical charge to the membranes are known as co-ions and are excluded from the membrane due to electroneutrality requirements (Strathmann, 2010). When selecting an IEM the most desired properties of them are high permselectivity, low electrical resistance, high mechanical strength and chemical stability (Nagarale et al., 2005). Permselectivity is of particular importance as it governs how well a membrane will reject the co-ions and has significant impact on process efficiency. With ideal characteristics, an IEM should be impermeable to the co-ions, have a low impact on overall stack resistance, and be able to withstand the physical and chemical conditions of the process along with any required cleaning procedures. In addition, the desired membrane properties need to be balanced with material and production costs (Nagarale et al., 2006).

Electrodialysis (ED) is a well-established IEM based electrochemical technology that utilizes IEMs and electric current to separate dissolved charged ions from a feed solution into a concentrated stream (Strathmann, 2010). In conventional ED processes CEMs and AEMs are arranged in an alternating order between two electrodes. The membranes are separated by spacers that create chambers that facilitate fluid flow between the membranes. Feed and concentrate solutions flow through the channels in an alternating order consistent with the membrane configuration. A combination of a CEM and an AEM along with a feed and concentrate streams are referred to as a cell pair. Using multiple cell pairs enhances ED performance with commercial ED stacks consisting of 100-200 cell pairs (Strathmann, 2010). During ED operation an electrical potential is applied between the terminal electrodes generating an electric field which creates a driving force allowing the ions to migrate towards the electrodes where water reduction and oxidation reactions are being driven. Reduction of water occurs at the cathode which results in the production of H_2 gas and OH^- ions while oxidation occurs at the anode which produces O_2 gas and H^+ ions. The cations in the feed migrate towards the cathode, and the anions migrate towards the anode removing ions from the feed channels and accumulating them in the concentrate channels. Figure 1.1 shows a diagram of a conventional ED process. Electrodialysis reversal (EDR) is a process based on conventional ED but involves reversing the polarity of the stack at regular intervals (Strathmann, 2010). EDR was developed in order to help control membrane fouling and it works by disrupting the layer of negatively charged organic foulants that have become attached to AEMs, allowing them to be removed from the membrane surface by convection. The addition of the reversal step has been shown to

have a significant impact on removing precipitated colloidal material and charged organics. Reversals generally take place over short term intervals and require more complicated flow control systems to accommodate the changing concentrate and diluate configurations (Strathmann, 2010).

An important factor to consider in an active ED system is concentration polarization and the resulting limiting current (Strathmann, 2010). In concentration polarization a boundary layer depleted of ions forms at the surface of the feed side of the IEMs which reduces the efficiency of the system as it becomes larger (Spiegler, 1971)(Kim, Walker, & Lawler, 2012). The boundary layer forms due to differences in the transport number between the counter ions and co-ions within the IEMs. As counter ions migrate through the membrane, the area adjacent to the feed side of the membrane becomes depleted of the counter ion and due to electroneutrality requirements the co-ions diffuse back into the bulk solution developing a boundary layer. With ion depletion the layer loses conductivity and a greater driving force is required to move ions into the boundary layer. Initially when increasing the applied voltage of the stack, the current will increase linearly according to Ohms Law, but as the increased resistance due to the boundary layer occurs, increases in voltage will not lead to significant increases in current. The value at which the current plateaus is known as the limiting current. Eventually with enough applied voltage the current will begin to increase again as water splitting occurs at the membrane surfaces. This is known as overlimiting current and while the mechanisms are not totally understood the water splitting can cause drastic shifts in pH, therefore most processes are operated at or below limiting current (Strathmann, 2010).

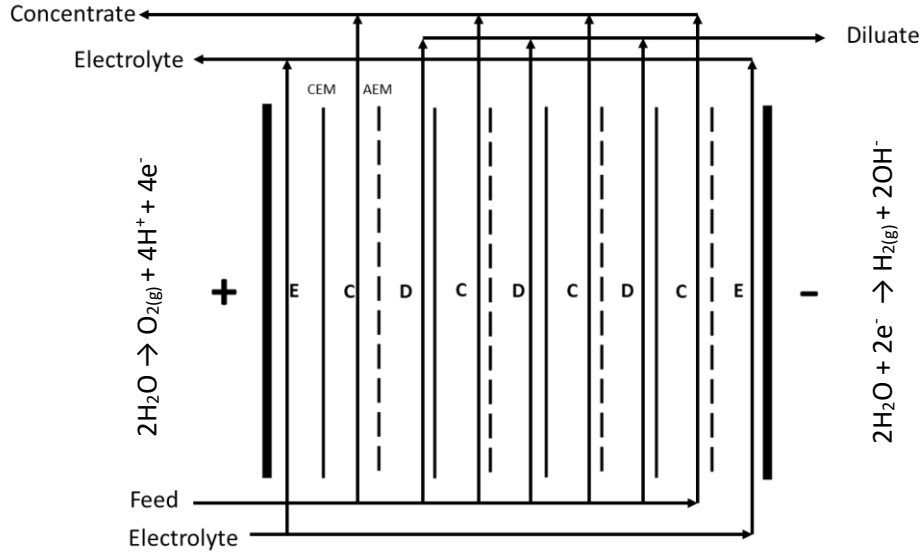


Figure 1.1 Diagram of a conventional electrodesalination process including membrane configuration and flow paths of concentrate, diluate and electrolyte streams.

1.2 Literature Review: nutrient separation from wastewaters using electrodesalination

While no full-scale applications of ED technology for wastewater nutrient separation are in use, a diverse set of wastewater streams have been evaluated at both bench and pilot scales and have shown promising recovery results. The nutrient rich wastewater streams that have currently been evaluated for ED processes include human urine, swine manure and anaerobic digestion centrate.

Urine streams are an excellent candidate for ED systems as urine is responsible for approximately 80% of the nitrogen and 50% of the phosphorous in raw wastewater (Larsen and Gujer, 1996). The recovery of nutrients from urine was first demonstrated by Pronk et al. (2006) and it was found that using a continuous lab scale electrodesalinator the separation efficiency of ammonia could reach 99% with product ammonia concentrations exceeding

13 g/L NH₃-N from an initial concentration of 4.85 g/L NH₃-N. The study also showed that water transport through IEMs poses a limitation to final product concentrations. Ammonia recovery from urine has also been demonstrated at pilot scale by Pronk et al. (2007). Pilot studies showed that stable ED operation could be achieved for 1-2 weeks with higher flowrates resulting in higher concentration factors. Performance decreases due to fouling was also monitored showing negligible decreases over 2 weeks of continuous operation and a 35% decrease in salt transport rate over a total of 195 days of operation. Overall source separated urine is an excellent candidate for nutrient recovery using electrodialysis with high recovery potential and manageable fouling effects.

ED has been evaluated by Mondor et al. (2008) and Ippersiel et al. (2012) to separate nutrients from manure and produce concentrated nitrogen fertilizer. Batch mode operation showed ED concentrate streams are able to reach a maximum of 16g/L NH₃-N from initial concentrations of 3.29g/L NH₃-N with ammonia transport rate limitations becoming an issue at 13-14g/L NH₃-N (Mondor et al., 2008). The maximum achievable ammonia concentration was limited by water transport into the concentrate and ammonia volatilization which shows that specific steps should be taken to minimize these effects for optimal ammonia recovery. The effects of IEM fouling are important to consider when using a high conductivity solution with high concentrations of organic macromolecules such as manure supernatant (Mondor et al., 2009). Fouling analysis showed that short term batch and continuous operation resulted in decreases in membrane electrical conductivity and ion exchange capacity with the largest issues being calcium carbonate (CaCO₃) scaling (Mondor et al., 2009). It was also shown that CEM performance could be completely

recovered using cleaning procedures, while AEM performance could only be partially recovered due to irreversible organic fouling (Mondor et al. 2009).

Following anaerobic digestion, anaerobic sludge is dewatered which produces a nutrient rich side-stream. Dewatering side-streams contain a high concentration of ammonia as well as many other organic and inorganic components that can make ED more complicated than conventional applications. The main treatment issue regarding dewatering side-streams is that after it is separated from the anaerobic biosolids, it is generally recirculated back to the headworks of the treatment plant. While dewatering side-streams account for small fraction of the total influent into the secondary treatment step, it can contribute up to 25% of the total nutrient load on the activated sludge system (Mbamba et al., 2016). By recovering the nitrogen in dewatering side-streams before recirculation, a high concentration nutrient product can be created while also decreasing the overall nutrient load on a plant. With high concentrations of recoverable ammonia and the potential to reduce the overall energy requirements, dewatering side-streams are an ideal candidate for nutrient recovery using ED. Nutrient separation from side-streams resulting from centrifugation (centrate) using ED has demonstrated consistent ammonia removal at both bench and pilot scale (Brewster et al. 2017) (Ward et al. 2018). Pilot experiments utilized centrate that was pre-treated with struvite crystallization to limit scale formation and were able to demonstrate effective ammonia removal reaching a maximum concentration of 7.9 g/L NH₃-N over a 72 h operation period with performance dropping after 24 h (Ward et al., 2018). The pilot research also showed that energy requirements for ammonia removal are well below that of conventional activated sludge systems and competitive with

ANNAMOX. Similar to the separation of nutrients from swine manure, the major challenge facing ED of dewatering side-streams is organic fouling and scaling which requires regular membrane cleaning in order to maintain effective process efficiency.

1.3 Literature Review: operational challenges with electro dialysis

One of the major problems with any membrane technology, especially when considering wastewater treatment applications is membrane fouling. In the case of electromembrane processes membrane cleaning is required keep the process operating efficiently and can account for up to 50% of total treatment costs (Grenenyuk et al., 1998). The three main categories of IEM fouling in ED are colloidal fouling, organic fouling and scale formation (Mikhaylin and Bazinet, 2016). Colloids are non-dissolved suspended solids such as clays and metal oxides and are found in natural and process waters. They have net surface charges that prevent flocculation and charge are influenced by the electric fields in ED. The charge also allows the colloids to interact with the charged groups of the membranes. Since most of the colloidal particles in wastewater are negatively charged, it is mainly the AEMs that are affected as the negatively charged colloid particles become attached to the positively charged ion exchange groups of the membranes (Mikhaylin and Bazinet, 2016). Organic fouling occurs when negatively charged organics become attached to the surface of the IEMS or within the matrix of the membranes (Mikhaylin and Bazinet, 2016). This type of fouling is especially important to consider as wastewaters generally contain high concentrations of organic compounds. Short term operation testing has shown that cleaning using high pH cleaning solutions is able to reclaim most of the performance

lost due to organic fouling of IEMs in wastewater applications, but the amount of irreversible fouling is likely due to organics that have become attached within the membrane matrix itself which cannot be removed through cleaning. In-depth analysis of the long-term impact organic fouling on IEMs in ED wastewater applications have not been completed (Brewster et al., 2017).

Scaling occurs when the concentration of low solubility salts exceeds its solubility limit and precipitates on the surface or within the membrane structure (Mikhaylin and Bazinet, 2016). Scaling is important to be able to predict and manage as it prevents the migration of ions through the membrane which significantly increases the stack resistance and therefore reduces the efficiency of the ED system. The main ions contributing to scaling in wastewater systems are Mg^{2+} , Ca^{2+} , PO_4^{3-} and HCO_3^- with CaCO_3 forming the vast majority of precipitation (Mondor et al., 2009) (Brewster et al., 2017). Most of the scale is in the form of CaCO_3 , and HCO_3^- species are more abundant than Ca^{2+} in dewatering side-streams, therefore Ca^{2+} is the limiting factor for precipitation. With Ca^{2+} as the limiting factor the majority of precipitation will occur where Ca^{2+} concentrations are the highest. As Ca^{2+} migrates through the CEMs a high concentration occurs at the surface of the concentrate side due to concentration polarization. Therefore, the majority of the scale will form on the surface of the concentrate side of the CEM. Scaling issues can be managed in wastewater applications of ED through pretreatment methods that remove scale forming ions such as struvite crystallization (Brewster et al., 2017) and by conducting acid membrane cleaning, which is able to dissolve the scale and restore performance to ED stacks (Mondor et al., 2009).

Water Transport from diluate into the concentrate stream has been found to be a significant factor in limiting product concentrations in ED nutrient recovery systems. Water transport occurs due to osmotic pressure between the concentrate chambers and the diluate chambers as well as the transport of solvated ions from electroosmosis, with electroosmosis being more dominant (Han et al., 2015). As water transfer dilutes the concentrate stream, the overall concentrations of desired products decrease, lowering the efficiency of nutrient recovery. The amount of water transport is dependent on the overall ion concentration and ion hydration numbers of the ions in the solution. Divalent ions present in high concentrations in wastewater such as Mg^{2+} and Ca^{2+} have higher ion hydration numbers and therefore contribute more to ED water transfer limitations. A model was developed by Pronk et al. (2006) in order to predict the amount of water transfer due to electroosmosis in urine ED systems.

In ammonia recovery applications using ED high concentrations of ammonia in the product can lead to significant losses due to volatilization. While ammonia in the form of NH_4^+ is non-volatile, NH_3 can be volatilized and lost. In order to control ammonia loss due to volatilization it is important to monitor pH levels to ensure that the pH is below the NH_4^+/NH_3 pKa (Ippersiel et al., 2012). Even with pH levels below the pKa value (9.25), as higher concentrations are reached in the ED concentrate stream ammonia is converted into its free form and volatilized. Experiments by Mondor et al. (2008) showed significant ammonia losses due to volatilization when approaching total ammonia concentrations of 13-14g/L while pilot experiments by Ward et al. (2018) showed losses of 28% over operation periods of 70h. With such large amounts of valuable product lost due to

volatilization, it is important to consider mitigation methods when considering the recovery of high ammonia product concentration such as using sealed concentrate reservoirs (Ippersiel et al., 2012).

1.4 Literature Review: ion exchange membrane cleaning

The two most significant types of fouling that impact ED of wastewaters are organic fouling and scaling, both requiring different types of cleaning chemicals to restore performance. The three main strategies for removing attached organics from membranes are using NaOH cleaning, free-chlorine based cleaning, and NaCl cleaning. NaOH cleaning solutions are the most common cleaning method for removing organics. Highly alkaline cleaning solutions are able to break down organics on the surface and within membrane. Alkaline cleaning solutions of 0.5-2% NaOH have been shown to be effective in recovering performance loss due to organic fouling in wastewater applications of ED (Mondor et al., 2009) (Pronk et al., 2007). NaCl has also been used in conjunction with high pH cleaning to help remove organics bound to IEMs by causing the desorption of bound foulants (Langevin and Bazinet., 2011). Oxidizers such as NaOCl have also been shown to control organic fouling of IEMs in wastewater applications (Ward et al., 2017). The use of oxidizers is very effective for breaking down organics, but has a significantly larger impact on membrane degradation than other cleaning solutions. Garcia-Vasquez et al. (2014) showed that the long-term usage of NaOCl resulted in the accelerated degradation of charged sites in AEMs. With more significant membrane degradation using oxidizers is not an ideal choice if aggressive cleaning is not required. While the majority of the impact of organic fouling can be mitigated using cleaning methods, there is a certain amount of

organic fouling that is irreversible even with extensive cleaning (Mondor et al., 2009). It is also important to note that not all AEMs are stable in high pH conditions, therefore membrane types should be selected carefully if high pH cleanings are expected to be required. Scale removal from IEMs is a relatively straight forward process where the precipitants are dissolved using an acid cleaning solution. Typically HCl and citric acid are used in making acid cleaning solutions. Cleaning solutions of 1% HCl or 6% citric acid have been shown to be effective in fully removing all the precipitants from wastewater electrolysers (Mondor et al., 2009) (Pronk et al., 2007). While chemical cleaning is an effective method to restore membrane performance due to fouling, the cleanings do have long term impact on membrane integrity. Garcia-Vasquez et al. (2016) demonstrated that cycling acid-base cleanings cause significant membrane degradation over 400-700 complete cycles. With membrane cleaning reducing the lifespan of the IEMs it is also important to look at fouling mitigation strategies instead of relying solely on chemical cleaning.

1.5 Research Objectives

The objectives of this study are to better understand nutrient recovery from dewatering side-streams using electrodialysis and evaluate methods to mitigate and recover the performance losses due to fouling. To further comprehend the challenges facing ED operation fouling rates under different condition were evaluated along with how much ED performance can be recovered with two stage cleaning procedures. Additionally, new ways to effectively characterize the contributions of organic and inorganic fouling were

developed by comparing the changes in stack resistance throughout membrane cleanings in order to improve understanding of fouling mechanisms.

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2. Fouling Control in Electrodialysis for Wastewater Applications

2.1 Introduction

With large amounts of recoverable nutrients throughout the wastewater treatment process, there is a shift in the industry to begin considering treatment plants as resource recovery facilities and focusing on identifying new resource recovery opportunities (Batstone et al., 2015). Liquid side-streams from anaerobic sludge dewatering processes are a small but nutrient rich stream with nutrient concentrations orders of magnitude larger than raw wastewater (Eddy et al., 2014). In most conventional treatment plants, dewatering side-streams are directly recirculated back to the beginning of the treatment process, contributing approximately 20% of the overall nutrient load (Mbamba et al., 2016). Conventional biological nutrient removal processes targeting ammonia ($\text{NH}_3\text{-N}$) are energy intensive and do not result in a recoverable nutrient product. Applying nutrient recovery technologies to concentrate side-streams would expand treatment capacity by reducing nutrient loads while also resulting in a valuable high concentration nutrient product.

Electrodialysis (ED) is an ion exchange membrane (IEM) based electrochemical technology that is used to separate ions in aqueous solutions, concentrating them into a single stream. ED processes consist of an alternating series of anion exchange membranes (AEM) and cation exchange membranes (CEM) positioned between two electrodes. When a voltage is applied across the membrane stack, an electric field causes ions to migrate towards the corresponding electrodes resulting in accumulation in the concentrate streams.

ED has conventionally been used for desalination, food processing and various chemical processes (Strathmann, 2010), but is not typically used for wastewater treatment.

The ability to separate ions from complex solutions makes the ED well suited for nutrient recovery from dewatering side-streams as ammonia is in its charged form (NH_4^+). Several studies have successfully demonstrated ED can recover nutrients from dewatering side-streams (Brewster et al., 2017)(Ward et al., 2018) and other wastewater streams such as human urine (Pronk et al., 2006) and swine manure (Mondor et al., 2008)(Ippersiel et al., 2012). Wastewaters pose a serious challenge to ED processes compared to conventional applications as they contain complex mixtures of organics and dissolved salts. The main limitation associated with using ED for wastewater applications is fouling of the IEMs. The two main forms of IEM fouling in wastewater ED applications are organic fouling and scaling. Organic fouling occurs when negatively charged organics build up on the surface or within AEMs. The organics can bind to the charged groups and inhibit anion migration. Scaling occurs when salt concentrations at the surface of the concentrate side of the IEMs exceed solubility limits and precipitate. The main scale forming ions in dewatering side-streams have been identified as Mg^{2+} , Ca^{2+} , PO_4^{3-} and HCO_3^- resulting in primarily CaCO_3 precipitation with smaller amounts of struvite (MgNH_3PO_4) as well (Brewster et al., 2017)(Mondor et al., 2009). Foulants can be removed by clean-in-place (CIP) procedures with different cleaning solutions targeting either organic fouling or scaling. NaCl Clean CIPs can be used to remove organic fouling by causing the desorption of bound organics, NaOH can also be used in conjunction with NaCl to help break down organics if the AEMs are stable at high pH conditions. Acid Clean CIPs are used to remove scaling as

the acid is able to dissolve the precipitated salts. Although scaling has been studied in-depth by scale formation models developed by Brewster et al., (2017), no work has been done assessing the combined contributions of organic fouling and scaling in centrate ED systems. Being able to quantify the contributions of both types of IEM fouling would be valuable as it would allow for better understanding of the causes of fouling and allow for more insight on how to mitigate the effects.

Various dewatering side-stream pretreatments have been used to mitigate some of the effects of fouling and scaling. Suspended solids can contribute to organic fouling as well as potentially obstructing the ED chambers. Ward et al. (2018) used settling and larger intermembrane spaces to mitigate these issues at pilot scale, but they are not ideal solutions as settling is a time and space intensive process and large intermembrane space reduces process efficiency. Screening is investigated in this study as a faster and more efficient option to remove suspended solids and reduce the chances of obstruction. With smaller suspended solids, smaller intermembrane distances can be used which improves ED efficiency. In order to reduce the severity of scale formation, struvite crystallization has been evaluated as another pretreatment (Brewster et al., 2017)(Ward et al.,2018). Struvite crystallization is an intensive pretreatment requiring chemical addition and long retention times. In addition, struvite crystallization also does not impact CaCO_3 formation which has been shown to be the most significant precipitant. Since only extensive pretreatments have been previously evaluated, in this study we determine if such intensive pretreatments are required and provide a systematic investigation on organic fouling and scaling. Previous studies also only considered constant current operation and did not look at the effect that

voltage has on fouling rate. More in-depth knowledge on the impacts of voltage on fouling will aid in determining optimal operational parameters.

The main objectives of this study are to better understand the effects of organic fouling and scaling on ED using dewatering side-streams. This will be accomplished by using real wastewater with minimal pretreatment and evaluating ED performance decreases over time. Additionally, the effectiveness of CIPs in recovering ED performance will be evaluated using a two stage, salt and acid CIP. The impact of applied voltage on the fouling rate will be also be assessed by comparing two electrolysers operating at different voltages and since organic fouling primarily impacts AEMs, the effects of fouling on two different AEM types will be compared as well. Additionally, a test method was developed to assess the different contributions of scaling and organic fouling to the overall increase in resistance due to fouling

2.2 Materials and Methods

2.2.1 Dewatering side-stream wastewater

Dewatering side-stream (Centrate) was collected directly from the anaerobic sludge centrifuges at a local wastewater treatment plant (Hamilton, Canada). Before ED operation the centrate was screened using a 0.3 mm sieve to remove large particulate solids and avoid potential spacer obstruction during ED operation. Centrate screening reduces TSS by approximately 30%. The pH (7.7 ± 0.1) and conductivity (9.64 ± 0.4 mS/cm) were consistent for the centrate collected throughout the study. The wastewater characteristics of the dewatering centrate are shown in Table 2.1.

Table 2.1: Average wastewater characteristics and ionic composition of centrate following screening pretreatment (n=3)

	mg/L	mM
Screened TSS	408 ± 39	-
sCOD	457 ± 29	-
NH ₃ - N	1053 ± 139	74.81 ± 9.87
PO ₄ - P	9.1 ± 0.5	0.29 ± 0.01
Na ⁺	142 ± 22	6.17 ± 0.95
K ⁺	81 ± 5	2.07 ± 0.12
Mg ²⁺	93 ± 8	3.82 ± 0.33
Ca ²⁺	51 ± 11	1.27 ± 0.27
Fe ³⁺	1 ± 0.5	0.02 ± 0.01

Centrate characteristic analysis consisted of measuring soluble chemical oxygen demand (sCOD), total suspended solids (TSS), ammonia (NH₃-N), phosphate (PO₄-P) were measured according to standard methods (APHA/AWW/WEF 2012). pH and conductivity were measured and logged using a bench-top meter (Orion Versa Star Pro, Thermo-Fisher, USA). Inductively coupled plasma spectrometry (ICP)(Vista Pro, Varian Inc., Australia) was conducted to measure cation concentrations of centrate samples. Sample preparation for ICP analysis consisted of acidifying the samples and filtration through a 0.45 µm syringe filter.

Particle size distributions (20 nm – 2 mm) of centrate solutions were measured using a particle size analyzer (Master sizer 2000s, Malvern Instruments, UK) The refractive index was set as 1.52 with and absorption of 0.1 for wastewater analysis (Sochan, Polakowski, & Łagód. 2014). Particle size analysis was completed on both raw and screened centrate samples.

2.2.2 Electrodialysis unit construction

Three bench-scale ED units were constructed and each electro dialyzer consisted of 4 CEMs and 4 AEMs arranged in alternating orders between two platinum coated titanium electrodes. The cation exchange membranes for all units were 0.38 mm thick CR67 membranes (Suez Water Technologies). Two ED units (4.5V AR908 and 7.5V AR908) contained 0.36 mm thick AR908 anion exchange membranes and the third electro dialyzer (4.5V AR204) contained AR204 AEMs (Suez Water Technologies and Solutions) (Table 2.2). Sheet flow path spacers (0.8-mm thick, ethylene-vinyl acetate) with a meshed open area of 36.75 cm² were used to separate the membranes and create a flow-path (Figure 4.1).

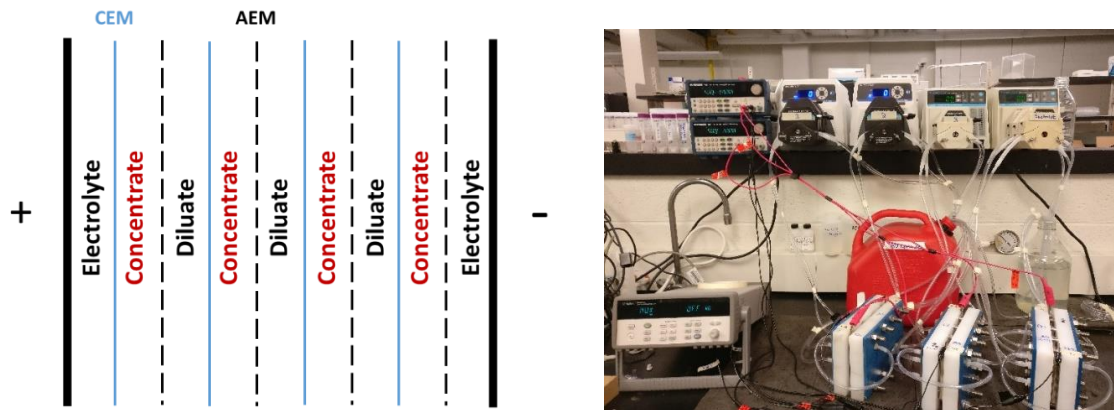


Figure 2.1: (A) Diagram of the electro dialyzer configuration including the polarity of the applied voltage and the arrangement of IEMs. Concentrate chambers are adjacent to the electrolyte chambers resulting in electrolyte migration into the concentrate chambers over time; (B) Experimental set-up of the 3 electro dialyzers along with the concentrate and electrolyte reservoir

This configuration results in 4 concentrate, 3 diluate, and 2 electrolyte streams (Figure 2.1 (A)). The electrolyte (50 mM Na₂SO₄) was pumped at 310 mL/min into the anode chamber before it flowed through the cathode channel to the reservoir. A higher flowrate for the electrolyte was used in order to prevent gas buildup in the electrode

chambers. The electro dialyzers were operated in Separate Flow or Combined Flow configurations depending on whether fouling experiments or performance baselines were being done (Figure 2.2).

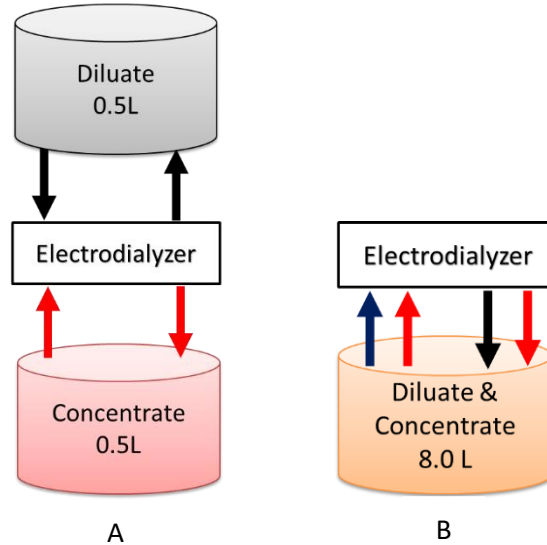


Figure 2.2: Diagram of both electro dialyzer flow configurations including flow path and reservoir volume: (A) Separate Flow configuration where diluate and concentrate flows utilize separate reservoirs for separation; (B) Combined Flow configuration where diluate and concentrate are returned to a shared reservoir preventing cumulative ion concentration.

2.2.3 Configuration for centrate fouling experiment

The three electro dialyzers were operated in Combined Flow configuration in parallel to each other. The Dewatering centrate was continuously recirculated through the ED units using peristaltic pumps (Masterflex L/S, Cole-Parmer, USA) at 170 mL/min (6 cm/s) from a shared 8 L reservoir (Figure 2.2 (B)). Combined Flow operation was run for 5-8 hrs each day and the electro dialyzers were flushed in both directions with 2 L of deionized water before storing in deionized water between experiment runs. Separate power supplies (9201, BK Precision, USA) applied 4.5 V to the 4.5V AR908 and the 4.5V

AR204 electrolysers and 7.5 V to the 7.5V AR908 electrolyser. During operation electric current was recorded at 5-minute intervals (3470A, Keysight Technologies, USA) and the electrolyte was replenished every 2 hours due to ion migration into the concentrate chamber. During the first 60 hrs of operation the electrolysers were run overnight which resulted in significant drops in current density as the electrolyte conductivity decreased due to ion migration into the concentrate chambers. For operation past 60 hrs, the electrolysers were operated and monitored during the day which resulted in significantly more stable current densities with only small decreases in current density between electrolyte replenishments.

2.2.4 Na₂SO₄ separation efficiency testing

Baseline tests were conducted initially, as well as before and after each CIP to monitor electrolyser performance. A Na₂SO₄ concentration of 50 mM was selected as it has a conductivity similar to concentrate. Three separate 500 mL reservoirs of Na₂SO₄ solution were used for the concentrate, dilute and electrolyte and recirculated. The electrolysers were operated in Separate Flow configuration (Figure 2.2 (A)) with a flow rate of 190 mL/min (6 cm/s) and 4.5V was applied to each unit for 45 min. Conductivity data of both concentrate and dilute reservoirs were recorded at 1-minute intervals (Orion Versa Star Pro, Thermo-Fisher, USA) and the electric current was recorded at 2-second intervals (3470A, Keysight Technologies, USA). The separation efficiency was calculated as the % removal of Na₂SO₄ from the dilute over the test period. Separation efficiency calculations used dilute removal instead of the concentration factor because ions from the electrolyte

also migrate into the concentrate chamber which would overstate the performance of the fouled membranes.

2.2.5 Centrate ammonia separation efficiency testing

Centrate separation testing is similar to the Na₂SO₄ separation efficiency testing, but used centrate as the concentrate and diluate instead of Na₂SO₄. The applied voltage was 4.5V to the 4.5V AR908 reactor and the test was run for 2.25 hrs to achieve 95% removal. Ammonia concentrations of both the concentrate and the diluate were measured initially and at 30-minute intervals for the first hour, then at 2-hour and 2.25-hour marks.

Table 2.2: Summary of operational conditions of each electro dialyzer for the fouling, Na₂SO₄ and centrate concentration tests. Centrate concentration tests were not done on 7.5V AR908 and 4.5V AR204 electro dialyzers.

	4.5V AR908	7.5V AR908	4.5V AR204
Fouling Configuration	Feed: Centrate Combined Flow (8 L) Applied Voltage: 4.5 V 5-8 hr/day (269 total)	Feed: Centrate Combined Flow (8 L) Applied Voltage: 7.5 V 5-8 hr/day (269 total)	Feed: Centrate Combined Flow (8 L) Applied Voltage: 4.5 V 5-8 hr/day (269 total)
Na ₂ SO ₄ Configuration	Feed: 50 mM Na ₂ SO ₄ Separate Flow (2 x 0.5 L) Applied Voltage: 4.5 V Test Length: 45 min	Feed: 50 mM Na ₂ SO ₄ Separate Flow (2 x 0.5 L) Applied Voltage: 4.5 V Test Length: 45 min	Feed: 50 mM Na ₂ SO ₄ Separate Flow (2 x 0.5 L) Applied Voltage: 4.5 V Test Length: 45 min
Centrate Concentration	Feed: Centrate Separate Flow (2 x 0.5 L) Applied Voltage: 4.5 V Test Length: 2.25 hr	-	-

2.2.6 Membrane cleaning procedures

CIP procedures were conducted when the electro dialyzers were no longer effectively separating ions resulting in low current densities. The first stage (NaCl Clean) of the CIP was designed to remove organic foulants by using a highly concentrated NaCl solution (50 g/L NaCl) either at neutral pH (4.5V AR204) or high pH (additional 50 g/L

NaOH)(4.5V AR908, 7.5V AR908). Note that AR204 membranes are not stable at high pH conditions (pH>10). The second stage (Acid Clean) was designated to remove precipitated scales using HCl (5% v/v). During each stage, the cleaning solution was recirculated at 75 mL/min for 2 hrs from 500ml reservoirs. Following each cleaning stage, the ED units were flushed with DI water to remove any residual cleaning solution. Following CIP procedures, the Acid Clean solution for each electrodialyzer was filtered and the Ca^{2+} , Mg^{2+} and Fe^{3+} concentrations were measured using ICP.

2.2.7 Fouling characterization using electrochemical impedance spectroscopy (EIS)

To better understand the effects of membrane fouling, a fast and non-destructive method was developed to quantify the contributions of organic fouling and scaling without having to remove membranes from the electrodialyzers. The NaCl Clean CIP targets organic fouling by disrupting and removing charged organics that have been bound to the AEMs while the Acid Clean CIP dissolves precipitated scale that has formed on the surface of the membranes. Differentiating between the organic and inorganic fouling was done by using EIS (VMP3, Biologic, France) to measure the stack resistance of the fouled electrodialyzers between cleaning stages and comparing the decreases in stack resistances achieved with each type of clean. The test defines the stack resistance reduction from the fouled stack resistance after the salt and hydroxide CIP as the organic contribution and the stack resistance reduction after the acid CIP as the inorganic scale contribution.

For EIS the anode of the electrodialyzers was selected for the working electrode and the cathode was the counter electrode. Prior to testing the ED units are flushed thoroughly with deionized water, and filled with electrolyte (50 mM Na_2SO_4). There is no

electrolyte flow for the test. During the EIS test, a single sine wave was applied at 0 V vs. the counter electrode with an amplitude of 10 mV through frequencies of 1 Hz-20 kHz. Stack resistance is then determined from the Nyquist plot (Figure 4.3).

2.2.8 SEM-EDS analysis of electro dialyzer scale

SEM-EDS (scanning electron microscopy-energy dispersive X-ray Spectroscopy) (JEOL, JSM-6610LV, Japan) analysis was done on scale samples from a separate centrate electro dialyzer. The analysis was completed to determine the physical and elemental characteristics of the scale that formed on the surfaces of the membranes.

2.3 Results and Discussion

2.3.1 Ammonia separation from centrate using electro dialysis

Applying 4.5 V for 2.25 hrs achieved 95% ammonia removal and the current density decreased at various rates throughout the test (Figure 2.3). The decrease in current density and therefore the decrease in the separation rate can be attributed to increasing concentration gradient between the diluate and concentrate, and the decreasing conductivity of the diluate. As the concentration gradient increases, changes in the separation rate can be observed around the 30 min and 60 min. The first 30 min of operation resulted in 32% ammonia removal and a 3% decrease in current density. The relatively stable current density shows that the concentration gradient did not play a significant role in limiting the separation rate up to 32% ammonia removal. Between 30-60 min of operation a further 23% of ammonia was removed with a 15% drop in current density. The decrease in current density is a result of the gradient beginning to have an impact on the separation rate after 55% removal. From 60 min to the end of the test 40% more ammonia separation was

achieved with a 53% drop in current density. The decrease is due to the concentration gradient and the low conductivity of the diluate streams having a significant impact on the separation rate resulting in much lower ammonia separation over the second half of the test. With separation rates dropping more rapidly after 55% removal, ammonia separation rates will be limited by the target separation efficiency, but even with significant drops in separation rates, ED was still able to reach nearly complete ammonia removal.

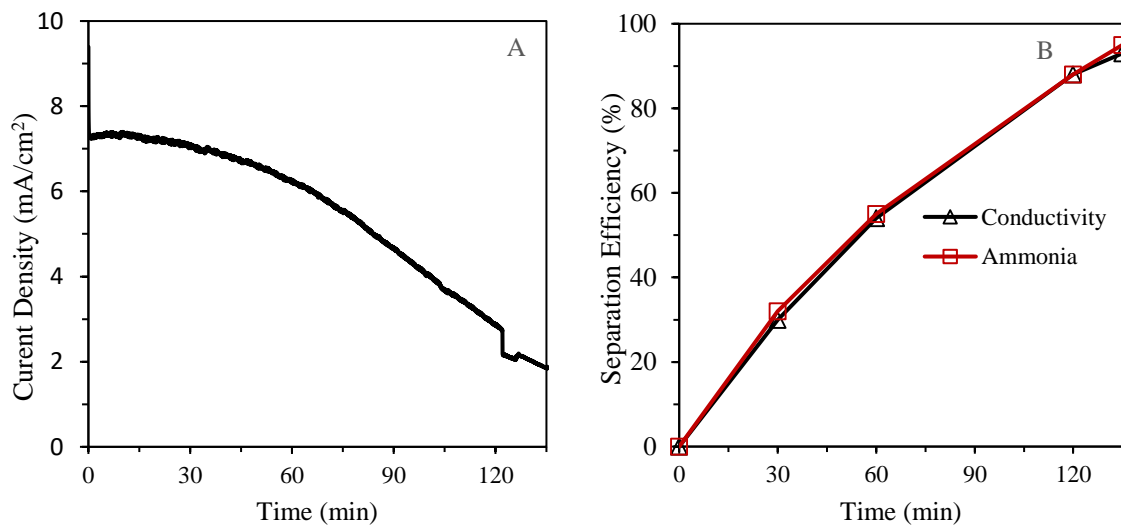


Figure 2.3: Current density and ammonia separation efficiency for batch centrate ED testing: (A) Current Density of the membrane stack; (B) Separation efficiency of conductivity and ammonia. Experiment was run over 2.25 h with constant 4.5 V applied in order to achieve a separation efficiency of > 90%.

The loss of ammonia due to volatilization is considered to be a limiting factor in ammonia recovery with the main factors affecting volatilization being atmospheric pressure and pH (Mondor et al., 2007). Ammonia losses were observed via potential volatilization (7% loss at 1 hr and 14% loss after 2.25 hrs) while concentrate reservoir pH was stable at 7.8 throughout the experiment. The losses occurred even though the final NH_3 fraction (pH 7.8) was only 3.4% of the total ammonia content. Ammonia losses at low NH_3

concentrations show that high ammonia separation efficiency can be limited by volatilization if the reservoir is open to the atmosphere. Volatilization losses could be minimized by maintaining a lower concentrate pH which keeps the equilibrium more in favour of non-volatile NH_4^+ (Ippersiel et al. 2012). Volatilization from ED concentrate can also present a possible recovery opportunity if the concentrate reservoir is sealed, as recovering gaseous ammonia through volatilization may be a viable purification method.

Water transport from diluate into the concentrate stream has been found to be a significant factor in ED separation of concentrated nutrient side-streams. Over 2.25 hrs of operation, the total amount of volume transfer from diluate to concentrate was 40 ml (8%). This result is consistent with previous high concentration ammonia ED separation studies and limits the maximum achievable product concentration due to dilution (Ward et al., 2018)(Mondor et al., 2007)(Pronk et al., 2006).

2.3.2 Rate of membrane fouling

Current densities for all electrolysers decreased throughout fouling testing, with higher applied voltage resulting in higher initial current densities and faster decreases in current densities (Figure 2.4). The decreases in current density are due to the increasing electrical resistances of the electrolysers due to membrane fouling. CIP#1(130 hrs) and CIP #2(190 hrs) were able to restore current densities to higher levels of all the electrolysers. High voltage application also resulted in less stable current densities than low voltage applications. Bubbles seen in the concentrate and diluate outlets suggest the instability is likely due to H_2 and O_2 gas from the electrolyte chambers leaking across the spacers and reducing the active surface area of the membranes before being flushed out.

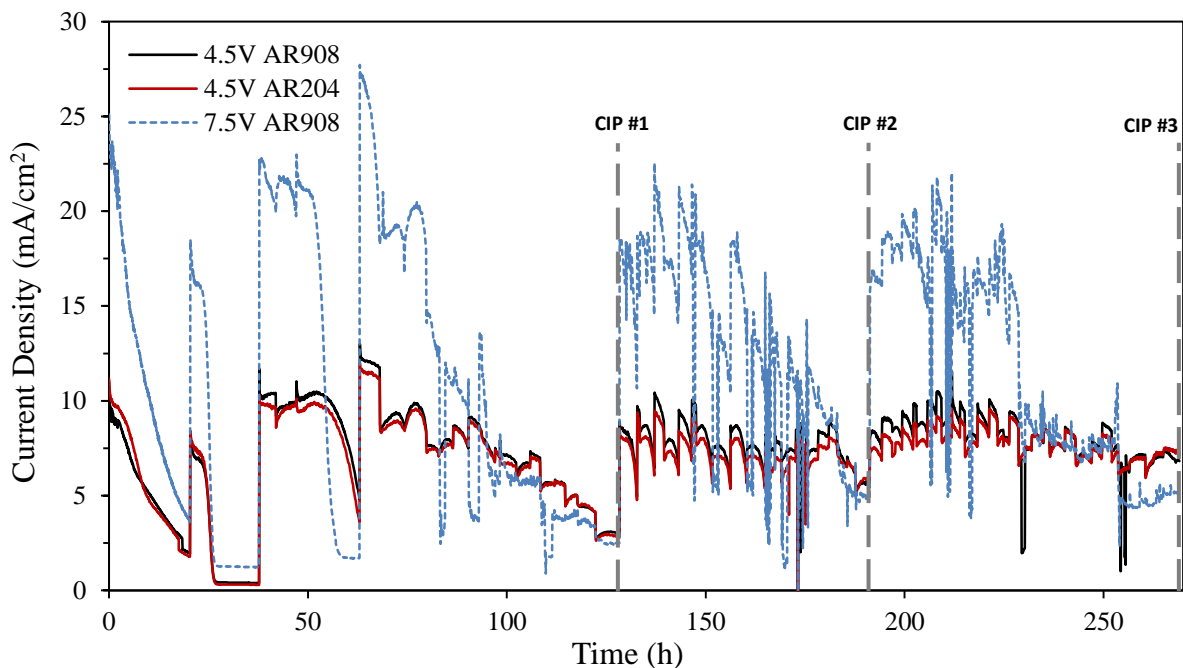


Figure 2.4: Long term electric current density data for the 4.5V AR905, 7.5V AR908 and 4.5V AR204 reactors over 269 hours of fouling testing showing CIP timings.

The degree of fouling was quantified using Na_2SO_4 separation efficiency over 45 min and showed that electro dialyzer performance decreased significantly over several days of operation due to fouling, with higher applied voltage resulting in more rapid fouling rates (Figure 2.5(A)). At low applied voltages, fouling resulted in 25-33% losses over 60-80 hrs of operation. CIPs are recommended at these intervals as longer operation would require oversized systems to handle the lower separation rates. Other wastewater membrane processes such as membrane bioreactors (MBR) typically require CIPs 1-2 times per week (Eddy et al., 2014), which shows that the fouling rate of the 4.5V AR908 electro dialyzer is not unreasonable for wastewater membrane processes, but could be improved. Ward et al. (2018) demonstrated pilot scale ED of centrate for 70 h operation runs between cleaning with only minor decreases in separation efficiency. The study was able to achieve longer

operation without major fouling since the centrate was pretreated using a struvite crystallization process. This suggests that utilizing pretreatments processes could be an effective way to reduce fouling rates and allowing for less frequent CIPs, reducing the operation costs of ED.

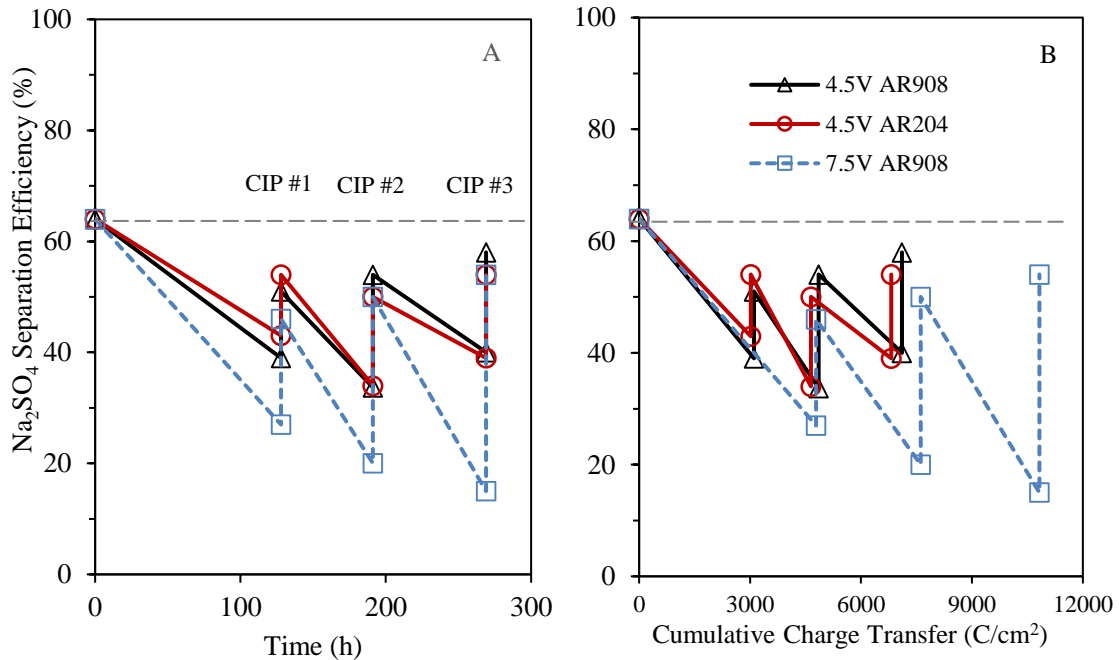


Figure 2.5: Separation efficiency test results for the 4.5V AR905, 7.5V AR908 and 4.5V AR204 reactors over 269 hours of fouling test operation showing the initial membrane 45-min Na_2SO_4 separation efficiency and the 45-min Na_2SO_4 separation efficiencies before and after CIP: (A) The separation efficiency changes over time; (B) The 45-min Na_2SO_4 separation efficiency changes with the cumulative charge transfer density

The more rapid drops in 45-min Na_2SO_4 separation efficiency for the 7.5V AR908 electrolysers demonstrates that the fouling rate is higher, but it is important to note that the 7.5V AR908 electrolysers also transferred more charge. When considering the cumulative amount of charge transfer, the fouling rate of high applied voltage was similar to that of low applied application (Figure 2.5 (B)). Similar cumulative charge density fouling rates suggests that using higher voltages will not have major negative impact ED

performance as long as CIPs are done more frequently to account for the process intensification.

2.3.3 Effectiveness of CIP procedures

CIPs were able to recover the majority ($85 \pm 4\%$) of the original separation efficiency of the fouled ED stacks (Figure 2.5(A)). The difference between the initial separation efficiency and the cleaned separation efficiency is due to irreversible fouling of the membranes. After the initial irreversible decrease in separation efficiency, the CIPs were able to consistently restore performance showing no further increases in irreversible fouling. Therefore, it is likely that after initial amount of irreversible fouling, the degree of fouling does not impact the effectiveness of CIPs. Mondor et al. (2009) observed similar irreversible fouling using ED to separate ammonia from swine manure. Analysis of the fouled membranes showed cleaned CEMs were able to reach original conductivity values after cleaning, while the AEMs had a persistent brown colour and were only able to reach 80% of their original conductivity. This suggests that the irreversible fouling is mainly impacting the AEMs in the stack. The study also found that scale was completely removed from the membranes during acid cleaning. This implies that the irreversible fouling is organic in nature. While the amount of irreversible fouling remained consistent throughout the 269 h of operation, it is possible that it will increase over longer operation and pilot studies are needed to quantify long term impacts. It is important to note that while the fouling rate over time for the 7.5V AR908 reactor was higher, it did not result in more irreversible fouling compared to the initial unfouled separation values. With no additional permanent impacts on the membrane observed over short term operation, higher applied

voltage appears to be viable option to increase process intensity as long as CIPs are done more frequently.

Using NaOH in addition to NaCl in the first cleaning stage did not result in a significantly greater separation efficiency recovery than using solely NaCl when comparing AR908 and AR204 membranes (Figure 2.5(A)). This shows that the ability of NaCl to affect electrostatic interactions and detach the bound organics from the AEMs could play a larger role in organic fouling removal rather than high pH.

2.3.4 Characterization of fouling

Monitoring stack resistance between CIP stages showed reductions in stack resistance between each cleaning stage (Figure 2.6 (A,B,C)). Decreasing stack resistances from both the NaCl Clean and Acid Clean stages show that CIPs are successfully removing both organic foulants and scale. Between the three CIPs scaling contributed on average to $63.3 \pm 5.3\%$ and $58.8 \pm 9.8\%$ of the total fouled stack resistance for the 4.5V AR908 and 4.5V AR204 electrolysers respectively. The relatively even split in fouling contributions showed that both organic fouling and scaling have significant contributions to IEM fouling, but scaling makes up a larger fraction overall. The significant contribution of organic fouling suggests that in addition to scale reduction pretreatments that target CaCO_3 or struvite precipitation, methods of reducing organic content will also play an important role in further decreasing fouling rates and CIP frequency. Brewster et al., 2017 developed a model to predict scale formation in centrate ED, but did not assess the contributions of organic fouling. The model only evaluates removing the major scaling ions (Ca^{2+} , Mg^{2+} , PO_4^{-3} , HCO_3^-) through pretreatment as the primary way of controlling ED fouling. The

significant contribution of organic fouling identified by the fouling characterization tests shows that organic fouling should be included in new fouling models in order to better predict ED fouling.

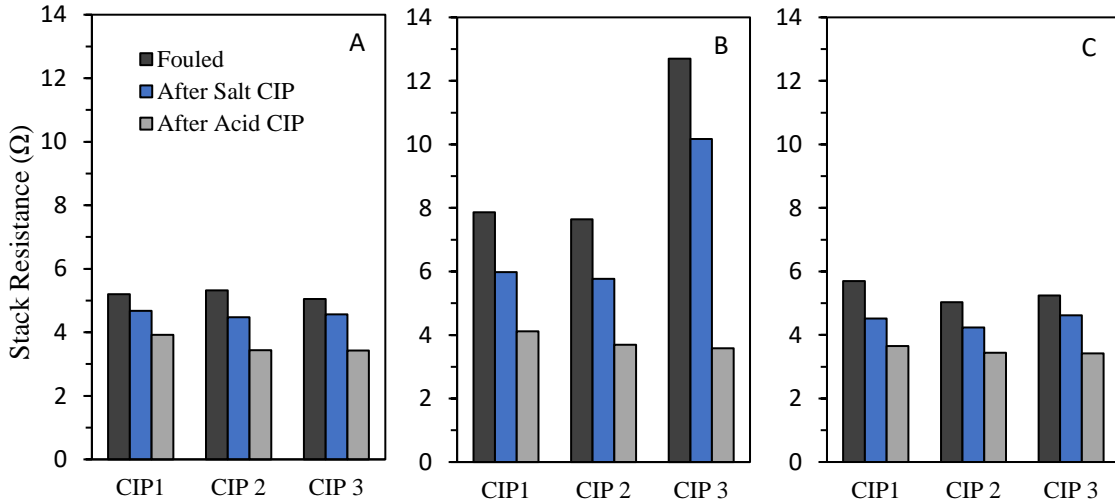


Figure 2.6: Stack resistance of the electrolysers before cleaning, after the NaCl Clean and after the Acid Clean for each CIP demonstrating the contributions of organic fouling and scaling to the overall fouled stack resistance: (A) 4.5V AR908; (B) 7.5V AR908; (C) 4.5V AR204.

ICP analysis of the Acid Clean solutions showed that the major cation present in the acid CIP solution is Ca^{2+} with smaller concentrations of Mg^{2+} and Fe^{3+} (Figure 2.7). High Ca^{2+} content in the cleaning solutions show that the scale formation is mainly due to the calcium precipitates while the smaller fraction of Mg^{2+} suggest some magnesium precipitation forming on the membranes as well. Small amounts of Fe^{3+} show that some iron precipitates are forming even with the low iron content (1 mg/L) of the concentrate feed. Within the concentrate chambers there are Cl^- and SO_4^{2-} ions which would allow for the precipitation of FeCl_3 and Fe_2SO_4 . Looking at the solubility limits in terms of mass percent of solute, FeCl_3 (47.7 at 25 °C) is significantly more soluble than Fe_2SO_4 (22.8 at

25 °C) therefore the iron precipitate on the membranes is likely in the form of Fe_2SO_4 (Haynes, 2014).

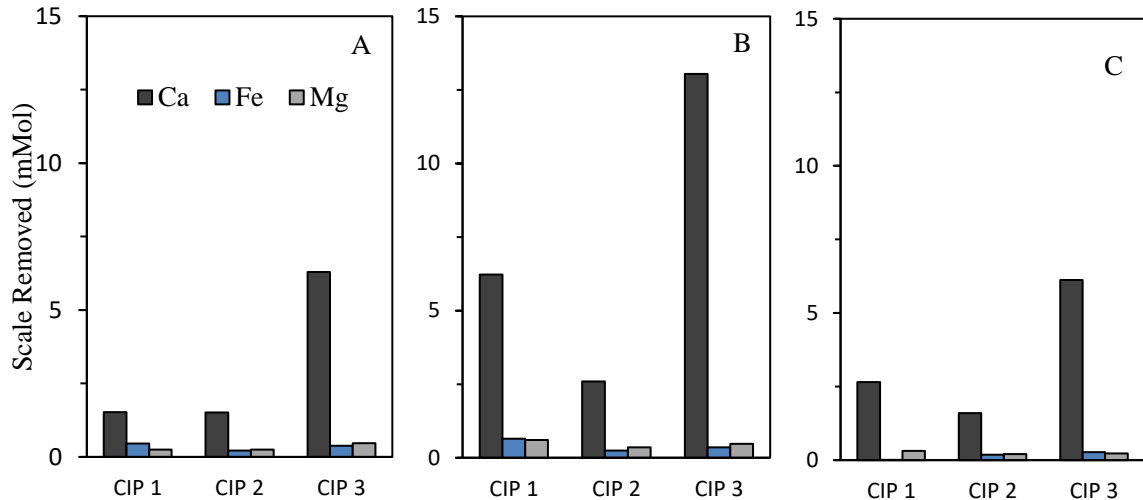


Figure 2.7: Mass of cations removed from the electrolysers during Acid Clean from each CIP: (A) 4.5V AR908; (B) 7.5V AR908; (C) 4.5V AR204

SEM-EDS analysis on scale formed in a separate centrate electrolysers showed that the scale did not form sharp crystals but did consist of a wide variety of sizes (Figure 2.8). Rounded crystals not likely to damage or puncture the membrane therefore scaling should not have major impacts on long term membrane integrity. SEM-EDS also showed high concentrations of C and O on the scale crystals with smaller traces of Mg and P throughout (Figure 2.9). The high concentrations of C and O show that the scale likely consists of mostly CaCO_3 while the Mg and P concentrations indicate that struvite is precipitating as well. The scale did not show localized crystal formation as the distribution of CaCO_3 and struvite appear to be uniform throughout the scale sample (Figure 2.10 (A, B, C, D)). The physical characteristics and scale composition are consistent with scaling

studies by Brewster et al. (2017) where CaCO_3 was determined to be the major cause of scaling. Even though the concentrate solution contains ample amounts of Mg^{2+} , NH_4^+ and PO_4^- the significantly smaller amount of struvite scaling is due to the pH of the concentrate stream (pH 7.8). The thermodynamic driving force of struvite precipitation does not become significant until a pH above 8.2 is reached, therefore struvite precipitation will be limited in the electrolysers since a constant pH below 8 is maintained during operation (Ali et al., 2005).

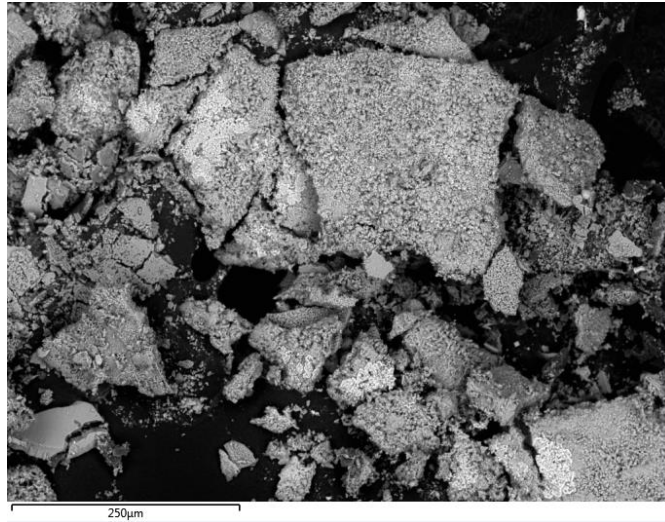


Figure 2.8: SEM photo of concentrate electrolysers scale showing the shape and size of inorganic scales that formed on the concentrate chamber side of the membranes.

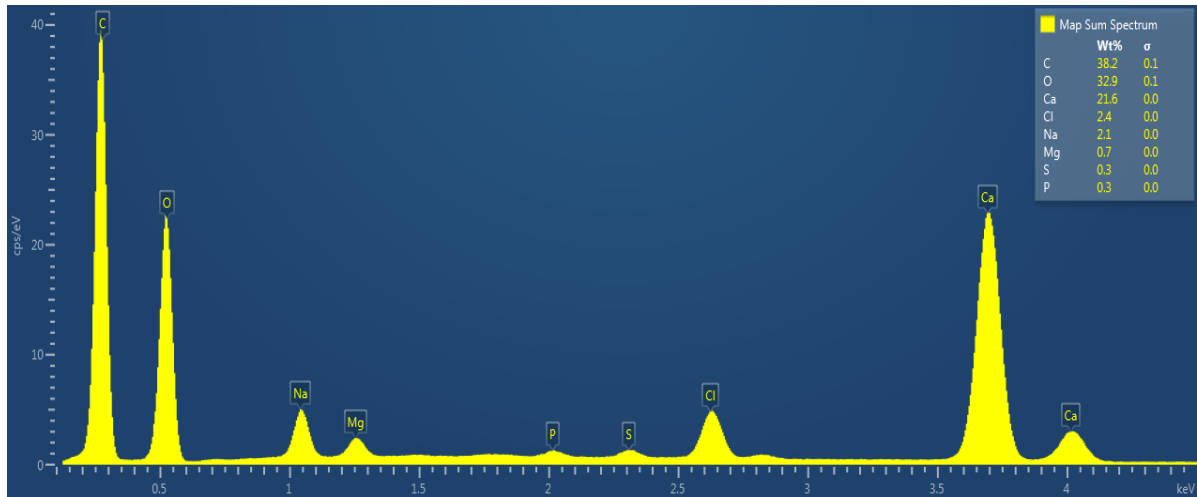


Figure 2.9: SEM-EDS results showing the elemental composition of the scale that formed on the concentrate chamber side of the membranes

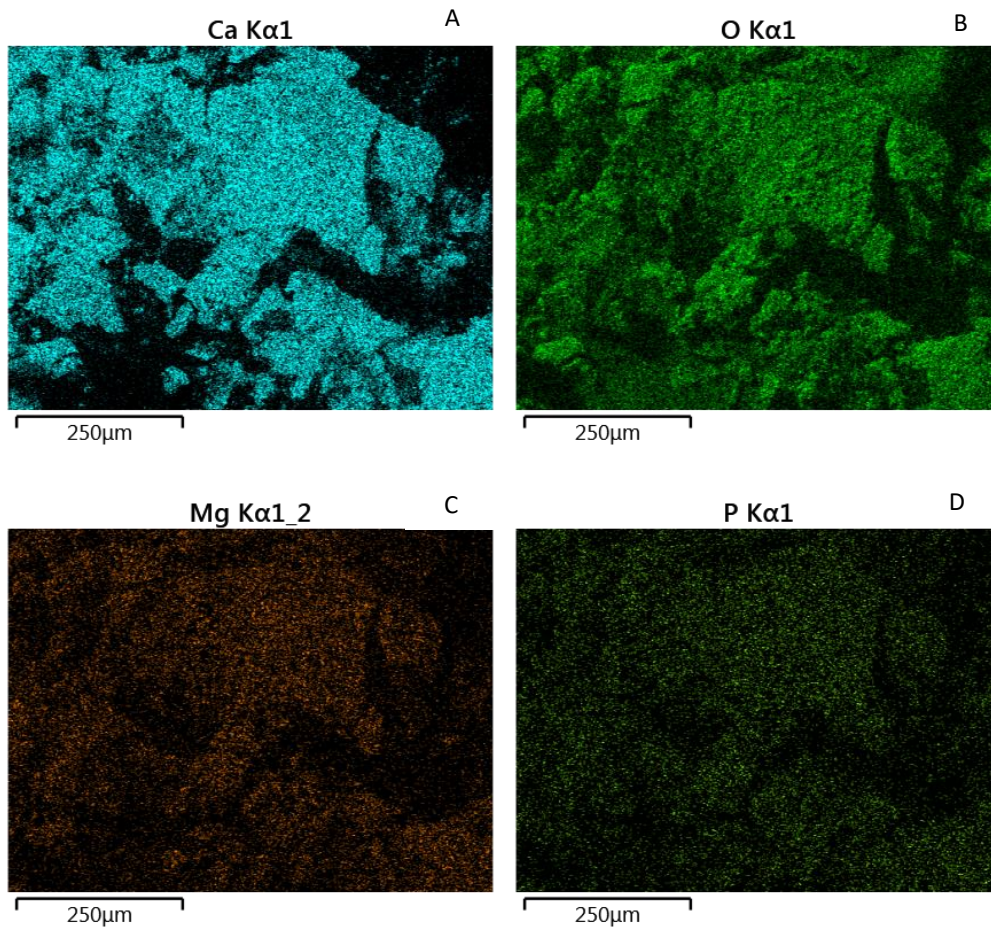


Figure 2.10: SEM-EDS element map analysis of scale formed in a centrate electro dialyzer: (A) Calcium; (B) Oxygen; (C) Magnesium; (D) Phosphorous

2.3.5 Comparison of AR908 and AR204 for Wastewater Applications

While performance between AR908 and AR204 AEMs are similar, the 4.5V AR908 electro dialyzer had marginally higher current densities than the 4.5V AR204 electro dialyzer throughout the fouling experiment (Figure 2.4). Higher current densities show that fouling seems to be having a larger impact on the AR204 AEMs compared to AR908. CIPs appear to be able to recover more of the initial performance for AR908 AEMs due to less irreversible fouling (Figure 2.5 (A)). Slightly more irreversible fouling found for the AR204 AEMs is likely caused by the absence of high pH during the NaCl Clean

CIP. While the irreversible fouling increase in AR204 AEMs is small at 269 hrs of operation, it is possible the irreversible fouling difference will increase over much longer periods of concentrate operation.

2.3.6 Pretreatment for suspended solids removal

Particle size distributions of raw centrate showed a wide range of particle sizes from 0.3 μm to $>2000 \mu\text{m}$ (Figure 2.10(A)). The distributions show that small particles make up the majority of the total particle volume, but there is still a notable fraction of larger particles. The larger particles, especially particles larger than the spacer thickness (800 μm) pose a challenge to ED operation as they are likely to get stuck in the spacer mesh and obstruct the concentrate and diluate chambers after several hours of operation (Brewster et al., 2017). To avoid the risk of obstruction the raw centrate was screened using a 0.3 mm screen. The screen pretreatment lowered the particle sizes such that 95% of the particles measured in screened samples were smaller than $275 \pm 69 \mu\text{m}$ (Figure 2.10 (B)). Screening effectively controlled particle sizes and no clogging issues were observed throughout the 269 hrs of operation of the 3 electrolysers. Other studies resolved this issue by using larger 6 mm thick spacers (Ward et al., 2018). The main issue with using larger spacers is that stack resistance is linearly proportional the distance between electrodes therefore larger spacers result in much higher overall stack resistances. Another issue is that large spacers reduce the turbulence at the surface of the membrane resulting in thicker concentration polarization boundary layers. Larger boundary layers significantly increase electrical resistance and reduce ED efficiency. Screening is a better solution than larger spacers as it

is a simple mechanical process and does not result in any increases in overall resistance.

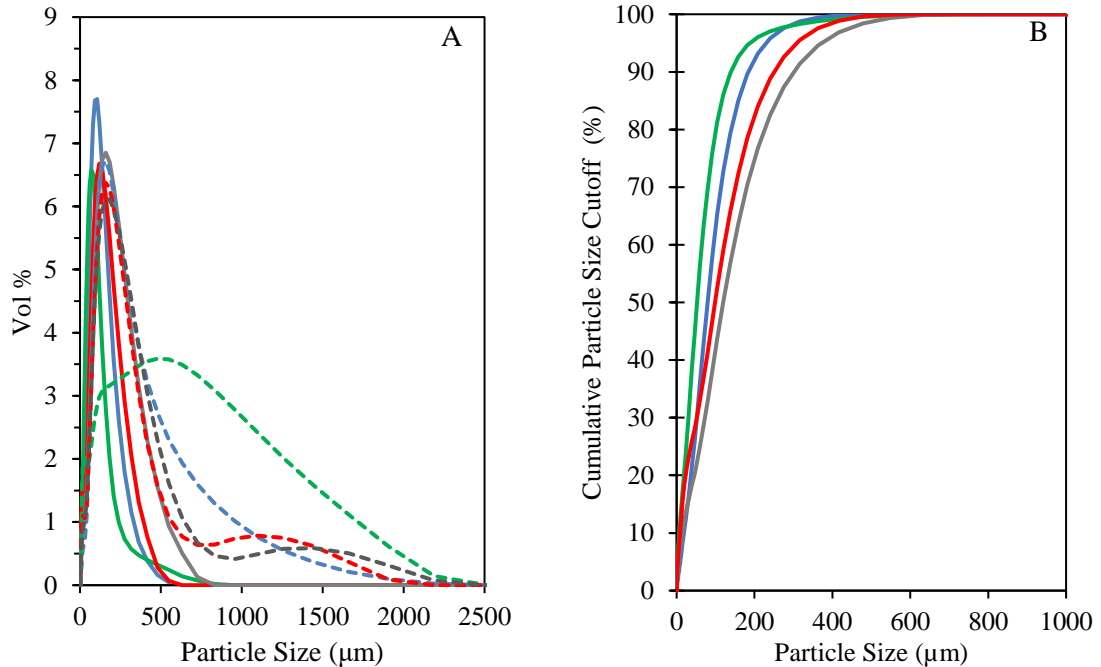


Figure 2.11: (A) Particle size analysis of 4 centrate samples before and after screening pretreatment. Dashed lines represent raw centrate distributions and solid lines represent the screened centrate distributions; (B) Particle size cutoff of 4 screened centrate samples showing the percentage of measured particles smaller than a given particle size

2.4 Conclusion

Using ED to recover nutrients from dewatering side-streams is an emerging application of the technology with the potential to produce high concentration nutrient products. Experimental work showed that ED was able to achieve 95% ammonia removal from centrate, while separation rates were limited by the concentration gradients between chambers and low diluate conductivity. Water transport due to electroosmosis and ammonia volatilization also proved to be factors that could limit maximum concentrate ammonia concentrations. Electrodialyzers were only able to run 60-130 hours before

significant losses in performance occurred due to IEM fouling. Operating at higher applied voltages resulted in higher separation but did not increase irreversible fouling. CIP procedures including NaCl Clean and Acid Clean stages were able to consistently restore $85 \pm 4\%$ of the initial membrane performance. The permanent decrease was due to irreversible fouling, which could not be recovered using CIPs. A fouling characterization test method was developed using stack resistances measured using EIS. The test method allows for membrane fouling characterization without having to remove membranes from the electro dialyzer. Fouling characterization showed scaling had a greater impact on membrane fouling with higher contributions to the overall fouled stack resistances. The scale that formed in the electro dialyzer chambers consisted of mainly CaCO_3 precipitation, with small amounts of struvite and iron precipitants. Particle size analysis of raw centrate presented potential spacer clogging issues due to large suspended solids. Using a 0.3 mm screen as centrate pretreatment resulted in no obstruction problems even with small spacer thicknesses. Results suggest that ED of dewatering side-streams is a viable process able to achieve high ammonia separation with reasonable cleaning frequencies, but pretreatments targeting scaling and organic fouling by reducing organic content and removing scaling ions such as Mg^{2+} , Ca^{2+} and HCO_3^- could further improve the process.

2.5 References

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3. Conclusions

3.1 Fouling control in electrodialysis for wastewater applications

It is important to look for innovative approaches to recover nutrients from wastewater in order to reduce the energy required for treatment and improve the sustainability of nutrient supplies. Anaerobic dewatering side-streams were selected as an ideal wastewater candidate for nutrient recovery using ED due to its high ammonia content and its significant contribution to plant nutrient load. Bench-scale electrodialyzer experiments resulted in 95% ammonia removal from a dewatering side-stream collected from centrifugation (centrate) and demonstrated that separation rates are limited by the concentration gradients between concentrate and diluate streams along with low conductivity of the diluate. Particle size analysis of the centrate presented potential issues due to spacer clogging, but screening pretreatment showed that stable operation could be achieved without increasing spacer thickness. Fouling proved to be the major challenge resulting in large losses in current density and ED performance over several days. The applied voltage proved to be an important variable in controlling fouling, with larger voltages resulting in faster fouling rates over time, but similar fouling rates when the cumulative charge transfer is considered. Two-stage cleaning procedures were able to recover most of the performance lost to fouling, but there was a persistent permanent loss due to irreversible fouling. A fouling characterization test was developed for differentiating between organic fouling and scaling. It showed that both organic fouling and scaling significantly contribute to overall fouling, but scaling had a larger impact overall. Results suggest that ED of dewatering side-streams is a viable process able to achieve high

ammonia separation with reasonable cleaning frequencies, but pretreatments targeting scaling and organic fouling by reducing organic content and removing major scale forming ions such as Mg^{2+} , Ca^{2+} and HCO_3^- could further improve the process.

3.2 Future Studies

3.2.1 Optimization of ED parameters

There are several key research opportunities to build on this research and further understand the impacts of fouling and develop effective mitigation strategies. Future work can include studies of the effects of more applied voltages on fouling. By evaluating more voltages, optimized operation parameters can be determined that balance higher separation rates with membrane fouling rates and improve ED efficiency.

3.2.2 Long-term fouling impact on membrane performance

In this study, the bench scale electrolysers only operated for a total of 269 h. While it was enough time to gain a preliminary understanding into the reversible and irreversible fouling effects of centrate on IEMs, significantly longer operation times are needed to fully understand the long-term impacts of fouling. Commercial ED systems will have to run continuously and the feasibility greatly depends on the long-term fouling effects on the membranes. A pilot study with larger electrolysers with fully automated controls could be used to operate over thousands of hours which would give a much better understanding of the long-term impacts of dewatering side-stream ammonia separation and if the technology will be viable in full scale applications. Long-term pilot operation using both AR908 and AR204 AEMs would also be valuable to confirm the similarity of the membranes over long operation times.

3.2.3 Dewatering side-stream pretreatments to mitigate fouling

Fouling characterization testing showed that both organic fouling and scaling have significant contributions to overall stack fouling. It would be valuable to further investigate centrate pretreatment options to mitigate fouling. Expanding on existing pretreatment work to include Ca^{2+} removal in addition to Mg^{2+} , PO_4^{3-} and HCO_3^- control would increase the effectiveness of scale focused pretreatments and reduce the competition for ammonia migration. Scale pretreatment topics could include the use of ion exchange resins or the addition of anti-scaling chemicals. Research into innovative methods of organic fouling control is also needed. This research could focus on removing soluble organics from the solution or modifying the charge of the organics to mitigate attachment to AEMs and reduce the impacts of organic fouling.

3.2.4 Optimization of CIP procedures

Cleaning chemical concentration in the two stage NaCl Clean and Acid clean procedure were recommended by the manufacturer and were not changed throughout all 3 CIPs. Further research optimizing the cleaning methods to determine the ideal concentrations and cleaning times would be valuable. Finding the minimum cleaning chemical concentrations that are still able to fully recover performance would help lower the costs of CIPs and identifying the ideal cleaning recirculation length would help reduce down time in full scale systems. Further work is also needed to determine if neutral pH NaCl cleaning is just as effective as high pH NaCl Clean, or if high pH is only required at certain intervals to maintain electro dialyzer performance. If NaOH addition is proven to not be necessary then Salt Clean procedures could be made simpler and cheaper.

3.2.5 Implementation of electro dialysis reversal to mitigate organic fouling

The electro dialyzers used in this study were only operated using the same polarity throughout the entire experiment. By implementing an electro dialysis reversal configuration organic fouling could be better mitigated. Further study is needed in order to evaluate how much reduction in organic fouling will occur due to polarity changes removing built up organics. This would be best achieved using an automated pilot on-site that is able automatically change polarity and flow paths throughout long-term operation. Polarity change intervals could be optimized to achieve the best fouling control while minimizing losses due to flow-path changes.

4. Appendix

4.1 Supporting figures



Figure 4.1: 0.8 mm thick sheet flow spacer constructed from ethylene-vinyl acetate used to separate membranes and create a flow path.



Figure 4.2: 0.3 mm screen used for pretreatment including the solids that were separated from 8L of centrate.

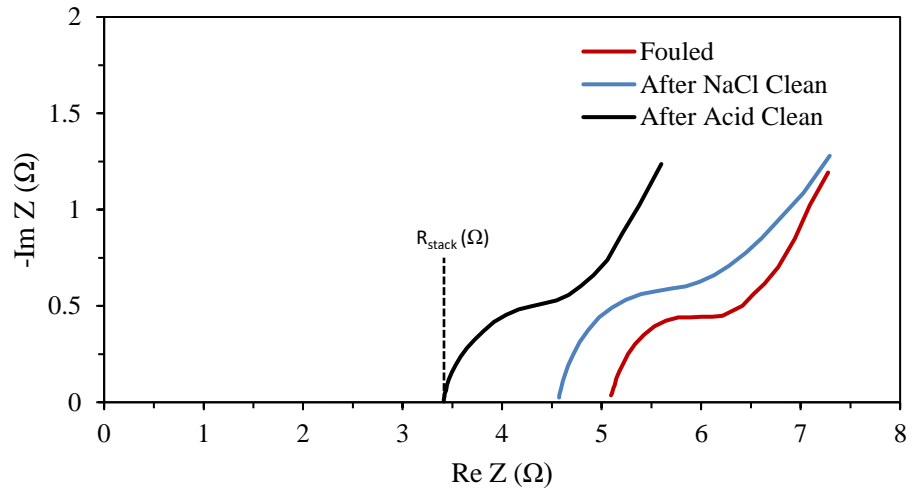


Figure 4.3: Nyquist plot of EIS results for an electro dialyzer throughout each stage of a CIP showing the decrease in stack resistance after the NaCl Clean and Acid Clean