Ammonia Recovery from Simulated Food Waste Liquid Digestate using Bipolar Membrane Electrodialysis

AMMONIA RECOVERY FROM SIMULATED FOOD WASTE LIQUID DIGESTATE USING BIPOLAR MEMBRANE ELECTRODIALYSIS

By:

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A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree of Master of Applied Science

McMaster University

2023

McMaster University MASTER OF APPLIED SCIENCE (2023) Hamilton, Ontario

(Civil Engineering)

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NUMBER OF PAGES: (53)

Abstract

Contamination of natural waters due to nitrogenous wastes has become a crucial environmental problem due to deterioration of water quality and eutrophication in aquatic eco-systems. Thus, the reduction of nitrogen accumulation in the natural environment is vital to maintain a healthy eco-system. Bipolar membrane electrodialysis (BMED) is a promising technology for selective ammonia separation from high-strength wastewater, such as liquid digestates of food waste or wastewater sludge. This technology was recently studied for reducing membrane scaling problems associated with conventional electrodialysis (ED) systems due to the water splitting mechanism in the BPM interface. A bench-scale BMED stack was built using 5 pairs of cation exchange membranes (CEMs) and bipolar membranes (BPMs). Using the BMED stack, a simulated food liquid digestate solution was examined to separate ammonia with different voltage applications and inter-membrane distances. The highest ammonia recovery was obtained at a cell pair voltage of 5.83 V (81% separation). Experiments on investigation of optimal inter-membrane distance of BMED operation suggested that the inter-membrane distance could be increased up to 2.46 mm without a significant decrease in nitrogen recovery. The residual Ca^{2+} and Mg^{2+} in the CIP (clean-in-place) solution which explains the degree of the scaling problem in the BMED was observed consistently below 2% of the initial mass introduced to the system, indicating that BMED design and regular CIP were effective in scaling control. The ammonia loss through CEMs to the feed cell by back diffusion was minimized due to high pH in the base cell since uncharged free ammonia was dominant over ammonium cation in the base cell. The energy required for BMED operation was comparatively low; 1.93-6.93

kWh/kg-N within 90 mins. Therefore, BMED can be considered as a sustainable candidate for selective ammonia recovery at high energy efficiency with successful scaling control.

Acknowledgements

Foremost, I would like to extend my most sincere and profound gratitude to my research supervisor Dr. Younggy Kim for his constant support and guidance throughout this arduous journey. Your insightful feedback and meticulous scrutiny inspired me to pursue my passion in wastewater engineering. I wouldn't have been able to complete this project if it wasn't for your infallible advice and patience.

I would also like to thank my other committee members for your valuable time. Further, I am grateful to John Barber, Vladimir Pavlovic and Pengyi Yuan for your support, knowledge and feedback which tremendously helped me in the completion of my project. Hui, thank you for being a very supportive and helpful mentor. Many thanks to Monica for helping me with everything in the lab throughout my research journey.

I would like to thank the Natural Sciences and Engineering Research Council of Canada, and Ontario Ministry of Research and Innovation for funding this research.

I am grateful to my dear friend Natalia for being a pillar of support throughout these two years. Sama, Sara and Ijaj, thank you for all your help. Last but not least, thank you Lalindra, my dear husband for being patient and supportive, my dearest mother and father who are miles away but kept me going everyday with their enormous love and support. Thank you Gayan and Guvanthi for all your help. Without you all, this wouldn't have been possible.

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List of Abbreviations

BMED	Bipolar membrane electrodialysis
ED	Electrodialysis
CEM	Cation exchange membrane
AEM	Anion exchange membrane
BPM	Bipolar membrane
IEM	Ion exchange membrane
CIP	Clean-in-place

Preface

Chapter 2 of this thesis consists of a paper to be published with multiple authors.

Dr. Younggy Kim, my research supervisor, together with Dr. Hui Guo guided me on the operation of bipolar membrane electrodialysis stack.

The bipolar membrane electrodialysis stack was constructed by me. The stack material was provided by the SUEZ company.

Pengyi Yuan, Vladimir Pavlovic and John Barber working in research and development at SUEZ provided me with an insight on the theoretical and technical aspects of electrodialysis.

The experiments were carried out by me and the manuscript for publication was written by me with the help of my research supervisor.

Chapter 1. Introduction

1.1 Nitrogen contamination

Nitrogen pollution is one of the pressing environmental concerns world-wide. Algal blooms which are formed due to eutrophication deteriorate water quality and aquatic life. Therefore, careful handling of nitrogenous waste is important in order to preserve the balance of the environment as well as to meet the strict nitrogenous waste disposal guidelines.

High strength wastewaters such as liquid digestate from food industry consists of high concentrations of nitrogen (<5000 mg-N/L) (Mohammadi et al., 2021) which requires mandatory treatment before discharge. However, such wastewater is a useful source for extraction of nitrogenous compounds such as ammonia which is a widely used chemical for agricultural productions in the world. Therefore, efficient separation of ammonia from high strength wastewater has gained a huge attention at present.

1.2 ED systems for resource recovery

The conventional wastewater treatment plants have not been built to sustain high nitrogen loading into the systems as it is highly energy consuming. Additional pumping and aeration costs must be incurred if these plants are designed to cater for the nitrogen load as dewatering centrate is directed back to the activated sludge system. This lowers the energy efficiency, also making the treatment process unsustainable.

Electrodialysis (ED) is a technology used for desalination (Had dad et al., 2019). Recently, ED has been applied for recovery of ammonia from wastewater. A conventional ED stack comprises cation exchange membranes (CEMs) and anion exchange membranes (AEMs) used to separate ions from diluate compartment to concentrate compartment. Significantly high ammonia concentration (>14 g-N/L) was achieved in previous studies conducted by Ippersiel et al. (2012) and Mondor et al. (2008) using swine manure. ED has its inherent disadvantages such as membrane fouling and scaling although these studies demonstrated high ammonia recovery. Membrane fouling is typically due to organic compounds (carbohydrates, proteins, aromatic substances, humic substances, oil, and antifoaming agents) found in wastewater (Lee et al., 2009; Tanaka et al., 2012). The electrostatic and hydrophobic forces attract these compounds to the IEM surface, specifically to AEMs (Jermann et al., 2007; Mikhaylin and Bazinet, 2016) as most of these foulants are negatively charged.

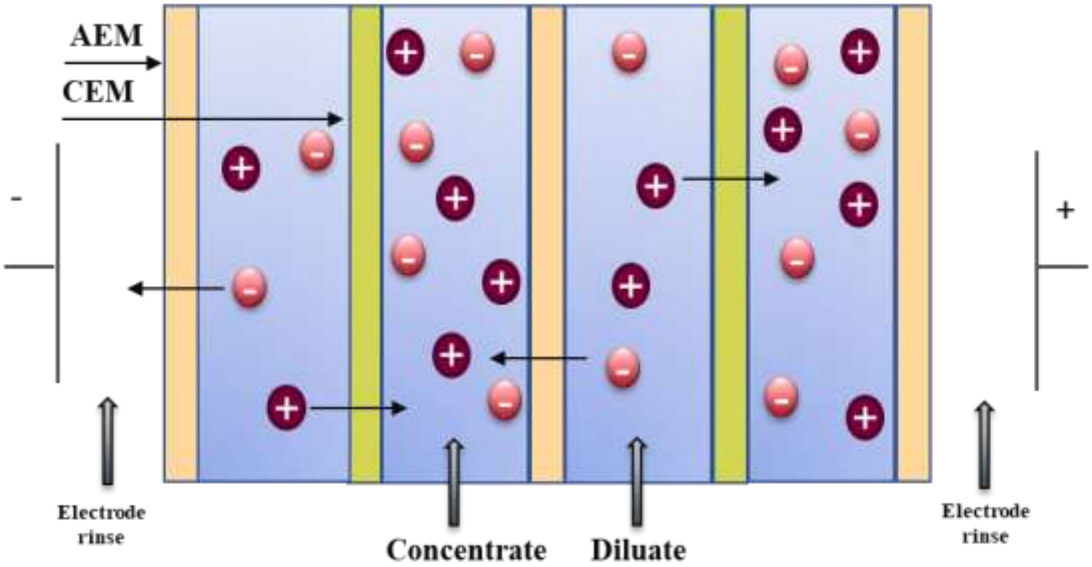

Figure 1.1 Conventional electrodialysis stack set up

Bipolar membrane electrodialysis (BMED) is a relatively new ion exchange technology that can be considered as an augmented form of ED. It is different from conventional electrodialysis systems due to the presence of bipolar membranes (BPMs). A BPM consists of an AEM and a CEM attached together (Alcaraz et al., 1998). Unlike other ion exchange membranes, BPMs do not allow passage of ions across the membranes while water is electro-dissociated into H^+ and OH^- in the biploar membrane junction forming a simultaneous acid and a base chamber. Successful research has been conducted using BMED for acid and base production (Bailly, 2002; Herrero-Gonzalez et al., 2020; Kumar et al., 2019; Lameloise and Lewandowski, 2012; Quoc et al., 2011; Zhang et al., 2011). Fu et al. (2014) reported manufacture of succinic acid using BMED with current efficiency over 90% and very low energy consumption (2.3 kWh/kg). Moreover, BMED technology has been applied recently for wastewater treatment industry (Gao et al., 2020; Tian et al., 2019) and recovery of ammonia using synthetic wastewater (Li et al., 2016; Van Linden et al., 2020). A BMED stack with five cell pairs using CEMs and BPMs were used in our study. A feed reservoir (1000 mL) of simulated food liquid digestate and a base reservoir of de-ionized water (250 mL) were used to separate ammonia from feed to base reservoir as ammonium hydroxide.

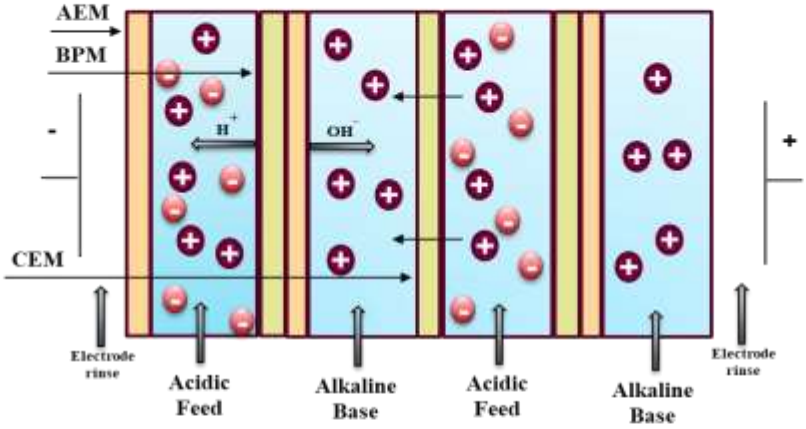

Figure 1.2 Bipolar membrane electrodialysis stack set up for ammonia recovery

1.3 Scaling in ED systems

Scaling is a major challenge in IEM processes including ED systems. Deposition of sparingly soluble salts such as carbonates, sulphates (Mikhaylin and Bazinet, 2016) or hydroxides of Mg^{2+} and Ca^{2+} on the IEM membrane pores and channels lead to scaling issues in ED operation. The overall performance of the ED system is negatively affected due to scale formation as separation and energy efficiencies become low with long term operation periods (De Paepe et al., 2018). The production of proton of the BMED system prevents the scale formation in the feed reservoir and the hydroxide production accelerates scaling in the base reservoir. Therefore, AEMs were replaced by Bipolar membranes (BPMs) to avoid scaling and fouling problems in conventional ED systems. Moreover, anion separation was of no interest in this study. Conventional ED systems fail to achieve maximum ammonia purity due to contamination of anions such as Cl^- and HCO_3^- which degrades the economic value of the final product (Guo et al., 2021). A special cleaning in place procedure (CIP) was carried out using HCl to control scaling since the simulated food liquid digestate solution comprised inorganic scalants in abundance (Guo et al., 2015; Wang et al., 2011). Quantification of cations contributing to scale formation was carried out to determine the degree of scaling in both feed and base channels during BMED operation.

1.4 Inter-membrane distance on ammonia recovery

A single cell pair of the BMED stack in this study consists of a feed compartment and a base (diluate) compartment separated by a CEM and a BPM. Spacers are placed in between the IEMs and BPMs to provide space for the solutions to flow inside the cell by maintaining the inter-membrane distance. Mixing of solutions in the cells is also facilitated due to the presence of spacers intensifying mass transfer by thinning the boundary layer (Kim et al., 2011; Zhong et al., 1983). Spacer thickness affects the stack resistance. The resistance of the BMED stack increases with increasing the spacer thickness (Kim et al., 2011). High conductivity of high strength wastewater (feed compartment) and production of hydroxides in the base compartment during BMED operation assist in overcoming the resistance created by spacers unlike conventional ED. Therefore, the inter-membrane distance can be larger for BMED operation in comparison to conventional ED. Moreover, Zhong et al. (1983) suggested the use of two spacers in order to increase the inter-membrane distance in practical electrodialysis applications. However, the effect of inter-membrane distance in BMED systems on ammonia recovery has not yet been studied. Thus, this study attempts to investigate the optimal inter-membrane distance of the BMED stack for efficient ammonia recovery.

1.5 Back-diffusion prevention in ED systems

Back-diffusion is another limitation in BMED operation (Li et al., 2016). The base reservoir in this study is concentrated four times than the feed reservoir. Thus, a steep concentration gradient developed over time inducing potential back diffusion of ammonium ions from base to feed which lowers the final concentration of ammonia in the base reservoir. The pH of the base reservoir during BMED operation becomes highly alkaline due to OH- production. As a result, ammonia is found as NH_3 in the base reservoir as the PKa of ammonia is 9.3 (Freney et al., 1981). The feed pH is neutral which indicates the presence of NH_4^+ ions. The hypothesis of less ammonia back-diffusion to feed from base was also investigated in this study due to alkaline pH in the base reservoir.

1.6 Research objectives

The research objectives in this study can be identified as

1. Investigating the optimal inter-membrane distance for efficient ammonia recovery
2. Investigating the effect of BMED design and clean-in-place procedure for scaling control in BMED
3. Recovery of ammonia minimizing back-diffusion

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Chapter 2 Ammonia Recovery from Bipolar Membrane Electrodialysis using Simulated Food Waste Liquid Digestate

Abstract

Contamination of natural waters due to nitrogenous wastes has become a crucial environmental problem due to deterioration of water quality and eutrophication in aquatic eco-systems. Thus, the reduction of nitrogen accumulation in the natural environment is vital to maintain a healthy eco-system. Bipolar membrane electrodialysis (BMED) is a great candidate in selective ammonia separation from high strength wastewater such as food waste liquid digestate. This technology also helps in reducing scaling problems associated with conventional electrodialysis (ED) systems due to the water splitting mechanism in the BPM interface. A bench-scale BMED stack was built using 5 pairs of cation exchange membranes (CEMs) and bipolar membranes (BPMs). A simulated food liquid digestate solution was used to separate ammonia over 90 mins operation time with different voltage applications. The highest ammonia recovery was obtained at a cell pair voltage of 5.83 V (81 %). The effect of inter-membrane distance of the BMED stack on efficient ammonia recovery, minimizing scaling was investigated in this study. The inter-membrane distance could be increased up to 2.46 mm without a significant decrease in nitrogen recovery. The percent residuals of Ca^{2+} and Mg^{2+} which were responsible for scaling in BMED were observed below 2% relative to initial mass introduced to the system indicating that regular CIP and BMED design were effective in scaling control. The ammonia loss through CEMs back to the feed reservoir was minimized due to high pH in the base since ammonia was available as free ammonia instead of ammonium ions. The

energy required for operation was comparatively low; 1.93-6.93 kWh/kg-N within 90 mins. Therefore, BMED can be considered as a sustainable candidate for selective ammonia recovery at high energy efficiency with successful scaling control.

2.1 Introduction

Anthropogenic discharge of nitrogenous compounds leads to adverse environmental effects including eutrophication which has become one of the pressing environmental concerns world-wide. Algal blooms formed due to eutrophication prevent penetration of oxygen and sunlight which ultimately results in deterioration of water quality and aquatic life. Therefore, prevention of eutrophication is important in maintaining a healthy aquatic eco-system (Li et al., 2021). This can be achieved by reducing the entry of nitrogenous waste into the environment. Moreover, the demand for nitrogen across the globe and stringent regulations on nitrogenous waste discharge to the environment can be met if nitrogenous compounds can be recovered from high-strength wastewater such as liquid digestate from food industry. Ammonium nitrogen is the biologically available form of nitrogen which is used to enhance agricultural production world-wide. Food waste liquid digestate contains a significant concentration of ammonia (>5000 mg-N/L). The Haber-Bosch process is currently employed for ammonia production which is energy-extensive and requires a significant carbon footprint as well (Guo et al., 2021; Li et ., 2021). Therefore, this study focused on efficient selective ammonia recovery as ammonium hydroxide in from simulated food liquid digestate with short operation time while achieving high purity.

A BPM consists of an AEM and a CEM attached together (Alcaraz et al., 1998). Bipolar membrane electrodialysis (BMED) has been widely applied for resource recovery from wastewater. BMED demonstrates high efficiency due to the ability of BPMs for simultaneous acid and base production as a result of water splitting at the BPM junction under the influence of an external electric filed (Mafé et al., 1998). Successful research has been conducted using BMED for acid and base production (Bailly, 2002; Quoc et al., 2011; Zhang et al., 2011; Lameloise and Lewandowski, 2012; Herrero-Gonzalez et al., 2020; Kumar et al., 2019). Fu et al. (2014) reported manufacture of succinic acid using BMED with current efficiency over 90% and very low energy consumption (2.3 kWh/kg). Moreover, BMED technology has been applied recently for wastewater treatment industry (Tian et al., 2019; Gao et al., 2020) and recovery of ammonia using synthetic wastewater (Li et al., 2016; Van Linden et al., 2020).

Scaling is a major challenge in IEM processes including ED systems. Deposition of sparingly soluble salts such as carbonates, sulphates (Mikhaylin and Bazinet, 2016) or hydroxides of Mg^{2+} and Ca^{2+} on the IEM membrane pores and channels lead to scaling issues in ED operation. The overall performance of the ED system is negatively affected due to scale formation as separation and energy efficiencies become low with long term operation periods (De Paepe et al., 2018). The production of proton of the BMED system prevents the scale formation in the feed reservoir and the hydroxide production accelerates scaling in the base reservoir. Therefore, AEMs were replaced by bipolar membranes (BPMs) to avoid scaling and fouling problems in conventional ED systems and also anion separation was of no interest in this study. Conventional ED systems fail to achieve maximum ammonia purity due to contamination of anions such as Cl^- and HCO_3^- which degrades the economic value of the final product (Guo et al., 2021). A special cleaning in place procedure (CIP) was carried out using HCl to control scaling since the simulated food liquid digestate solution comprised inorganic scalants in abundance (Guo et al., 2015; Wang et al., 2011). Quantification of cations contributing to scale formation was carried out to determine the degree of scaling in both feed and base channels during BMED operation.

A single cell pair of the BMED stack in this study consists of a feed compartment and a base (diluate) compartment separated by a CEM and a BPM. Spacers are placed in between the IEMs and BPMs to provide space for the solutions to flow inside the cell by maintaining the inter-membrane distance. Mixing of solutions in the cells is also facilitated due to the presence of spacers intensifying mass transfer by thinning the boundary layer (Kim et al., 2011; Zhong et al., 1983). Spacer thickness affects the stack resistance. The resistance of the BMED stack increases with increasing the spacer thickness (Kim et al., 2011). High conductivity of high strength wastewater (feed compartment) and production of hydroxides in the base compartment during BMED operation assist in overcoming the resistance created by spacers unlike conventional ED. Therefore, the inter-membrane distance can be larger for BMED operation in comparison to conventional ED. Moreover, Zhong et al. (1983) suggested the use of two spacers in order to increase the inter-membrane distance in practical electrodialysis applications. However, the effect of inter-membrane distance in BMED systems on ammonia recovery has not yet been studied. Thus, this study attempts to investigate the optimal inter-membrane distance of the BMED stack for efficient ammonia recovery.

Back-diffusion is another limitation in BMED operation (Li et al., 2016). The base reservoir in this study is concentrated four times than the feed reservoir. Thus, a steep concentration gradient developed over time inducing potential back diffusion of ammonium ions from base to feed which lowers the final concentration of ammonia in the base reservoir. The pH of the base reservoir during BMED operation becomes highly alkaline due to OH- production. As a result, ammonia is found as NH_3 in the base reservoir as the PKa of ammonia is 9.3 (Freney et al., 1981). The feed pH is neutral which indicates the presence of NH_4^+ ions. The hypothesis of less ammonia back-diffusion to feed from base was also investigated in this study due to alkaline pH in the base reservoir.

2.2 Materials and Methods

2.2.1 Setting up the BMED

A bench-scale BMED stack (Figure 2.1) was constructed using 5 CEMs (CR62, SUEZ Water Technologies & Solutions, Canada) and 5 BPMs (AR103 and CR61, SUEZ Water Technologies & Solutions, Canada) (Guo et al., 2021; Mohammadi et al., 2021). An extra AEM (AR 103, SUEZ Water Technologies & Solutions, Canada) and a CEM (CR62, SUEZ Water Technologies & Solutions, Canada) were placed near the anode and cathode chambers respectively to prevent the transfer of ions in the feed reservoir to electrode rinse reservoir. The BMED stack consisted of feed and base channels (Figure 1) as acid stream was not present due to lack of AEMs. Inter-membrane distance in the stack was maintained using polyethylene mesh spacers with an effective IEM surface area of 36.7 cm^2. Titanium plates coated with platinum were used as electrodes. The physiochemical properties of IEMs are shown in Table 2.1.

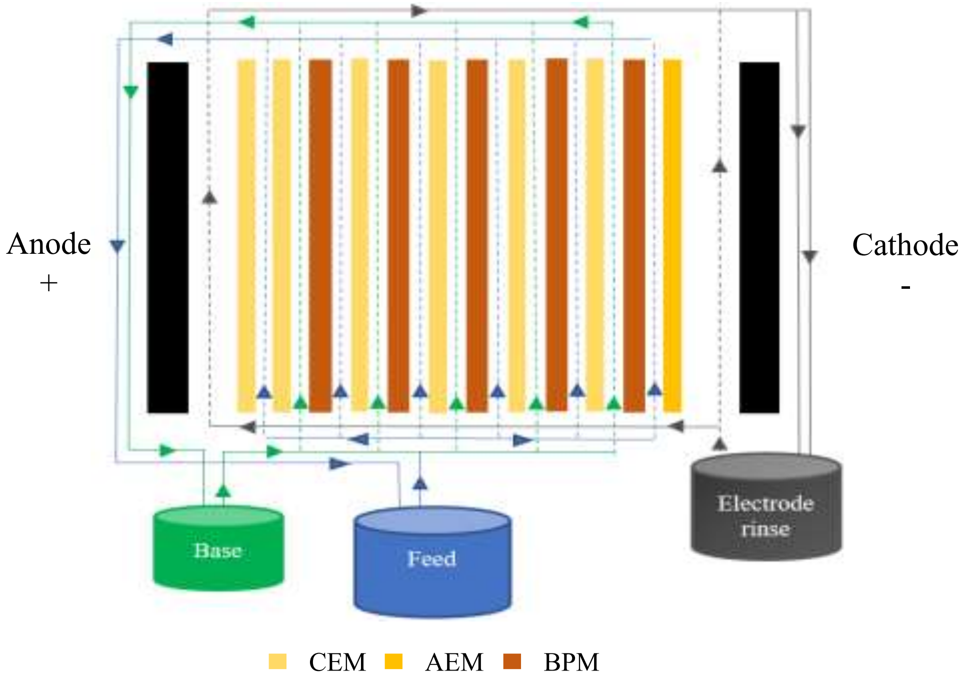

Figure 2.1 BMED Stack

Table 2.1 Membrane properties (supplied by the manufacturer)

	CR 62T	AR 103 N	BPM
Thickness (mm)	0.32	0.38-0.42	1.1
Burst strength (psi)	85	95	
Ion-Exchange Capacity (meq/dry gram membrane)	2.60	2.37	
Resistivity (in 0.5 N NaCl at 25 °C) (Ω-cm^2)	6	3.48	
Permselectivity (%)	97	92	
pH operation range	1-14	1-14	1-14
Maximum current density (mA/cm^2)	32.5	32.5	32.5

2.2.2 BMED operation

The system was operated using an electric filed provided by anode and cathode which were connected to an external power supplier (Model 9201, BK Precision, USA).

Table 2.2 Composition of the feed solution

Parameter	Average and Standard deviation	Reference
Ammonium chloride	5000.00±0.001 mg N/L	Maya-Altamira et al., 2008
Calcium chloride	88.78±0.001 mg/L	Kurup et al., 2019
Magnesium chloride	95.21±0.001 mg/L	Diamantis and Aivasidis, 2018
Sodium bicarbonate	8400.00±0.001 mg/L	McGarvey et al., 2005
Sodium chloride	409.08±0.001 mg/L	El-Fadel et al., 2002
Potassium chloride	149.10±0.001 mg/L	McGarvey et al., 2005
pH	7.86±0.049	-
Conductivity	49.11±0.276 mS/cm	-

A synthetic feed solution representative of liquid digestate from food waste was prepared in the lab. The composition used for preparation is given in Table 2.2.The BMED operation was carried out with 1 L of synthetic feed solution, 250 mL of deionized water as the base reservoir to recover ammonium hydroxide with maximum purity. A volume of 1 L of 0.1 M Na_2SO_4 was used as the electrode rinse solution. The system was operated for 90 minutes allowing recirculation of all three solutions using peristaltic pumps which were connected separately to each reservoir. Deionized water was circulated in the stack prior to starting the experiments for five minutes to eliminate the air bubbles trapped inside. The linear velocity of the feed and base channel was maintained throughout operation at 1.61 mL/min and the electrode rinse at 4.65 mL/min. Duplicated experiments were performed at five different voltages (Figure 2.2) by varying the inter-membrane distance in the feed chamber from 0.82,1.64, to 2.64 mm using the polyethylene mesh spacers while maintaining constant linear velocity in the feed channel accordingly.

2.2.3 CIP (clean-in-place)

Clean-in place procedure (CIP) was carried out by using 5% HCl followed by 5% NaCl for 30 minutes by alternating the flow direction every 15 minutes. The BMED stack was cleaned using 6 L of deionized water before and after the CIP.

The cations in the CIP samples from feed, base, and electrode rinse during the experiments with 2.46 mm series were quantified to investigate the scaling in the chambers. Each chamber was rinsed first using 1 L of Deionized water followed by cleaning with 5% HCl twice (CIP 1 and CIP 2). Samples were collected from feed, base, and electrode rinse reservoirs from CIP 1 and 2.

2.2.4 Voltage drop per cell pair

The voltage drop at the electrodes was found by assembling a stack with the electrodes, 1 CEM, and 1 AEM. The reservoirs used were feed (1 L of synthetic solution) and electrode rinse (1 L of 0.1 M Na_2SO_4) only. The voltage applied was increased every three minutes and the average current was found (Figure S3). The cell pair voltage was found using equation 1 and is presented in Figure 2.2.

$$\text{Cell pair voltage drop (V)}=\frac{E^{total}-E^{electrodes}}{\text{Number of cell pairs}} \qquad \text{Eq 1}$$

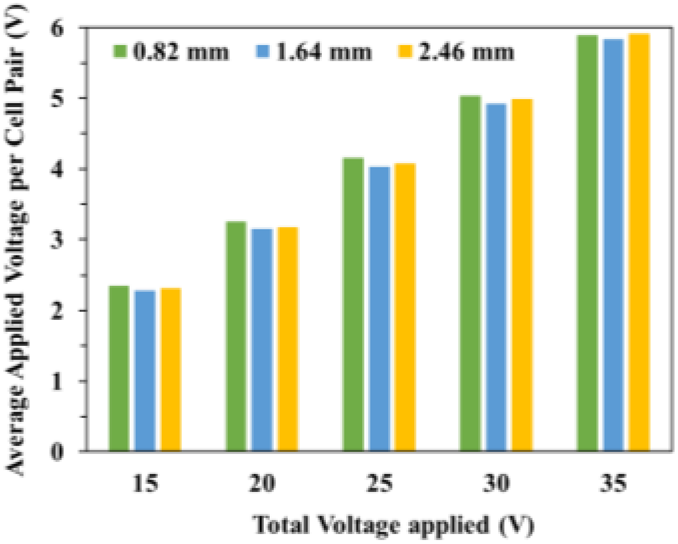

Figure 2.2 Average applied voltage per cell pair with total voltage applied to the BMED stack

2.2.5 Back-diffusion experiments

Five bench-scale reactors were built using polypropylene blocks. A single reactor was built by placing a CEM (CR62, SUEZ Water Technologies & Solutions, Canada) in the middle of two blocks. The feed and base sides of the reactors were filled with 15 mL of the solutions provided in Table 2.3. In reactors 1-3, the feed pH was changed, and the base pH was kept constant simulating the pH at the end of voltage application experiments. In reactors 4 and 5, pH of the base side was changed while the pH of the feed was kept constant. The reactors were allowed to sit for 90 minutes without providing electricity. Ammonia concentration in the feed side was measured every 30 minutes.

Table 2.3 Chemical composition of feed and base sides of the reactors used in back-diffusion experiments

Test	Feed	Base
Test 1	0.4M HCl	0.357 M NH_4OH
Test 2	0.4M NaCl	0.357 M NH_4OH
Test 3	0.4M NaOH	0.357 M NH_4OH
Test 4	$NaHCO_3$[a]	0.357 M NH_4Cl
Test 5	$NaHCO_3$[a]	0.357 M NH_4OH

a: The pH was maintained at 6.7 to simulate the feed pH of at the end of voltage application experiments

2.2.6 Experimental analysis

Experimental measurements such as pH, conductivity (Orion Versa Star, Thermo Scientific, USA) and ammonia concentration (Ammonia test kits, Method 10205, Hach Company, USA) were obtained at 0,30,60,and 90 minutes in the feed and base samples collected from voltage application experiments. The samples (including CIP 1 and 2) were further analyzed using Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES, Vista Pro, Varian Inc., Australia) for other cations namely Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}. Prior to ICP-OES analysis, the samples were treated with 70% nitric acid (W/W) and then filtered using syringe filters with a pore size of 0.45 μm (polyethersulfone membrane, VWR

International, USA). Samples from the feed reservoirs in each reactor were collected at intervals 0f 0, 30, 60, and 90 minutes from the back-diffusion experiments. Ammonia (Ammonia test kits, Method 10205, Hach Company, USA), pH (Orion Versa Star, Thermo Scientific, USA) and conductivity (Orion Versa Star, Thermo Scientific, USA) of the samples were measured.

2.2.7 Energy requirement

The energy requirement (KWh/kg-N) of the BMED stack was calculated using the following equation (Eq 2). The energy pertaining to pumping is not considered as it is relatively low in comparison to the energy used for voltage applications in BMED (Strathman, 2004).

$$\text{Energy consumption} = \frac{\Sigma\, E^{\text{applied}}\, I_t \Delta t}{3600 \times (C_{F0}V_{F0} - C_{Ft}V_{Ft})} \qquad \text{(Eq 2)}$$

$E^{applied}$ (V) was the voltage applied for single experiment, I_t (A) was the electric current at time t, and Δt (s) was the time interval. C_{F0} (kg/L) and C_{Ft} (kg/L) were the free ammonia concentration in the feed solution at time 0 and t. V_{F0} (L) and V_{Ft} (L) were the volumes of the feed solution at times 0 and t.

2.3 Results and discussion

2.3.1 Effect of applied voltage on current density

The highest current density (23.9 mA/cm^2) was obtained in 1.64 mm series (Figure 2.3). Current density increased linearly with the applied voltage (Figure 2.3) from 15 to 35 V. Similar current densities were found for the inter-membrane distances of 0.82 and 1.64 mm

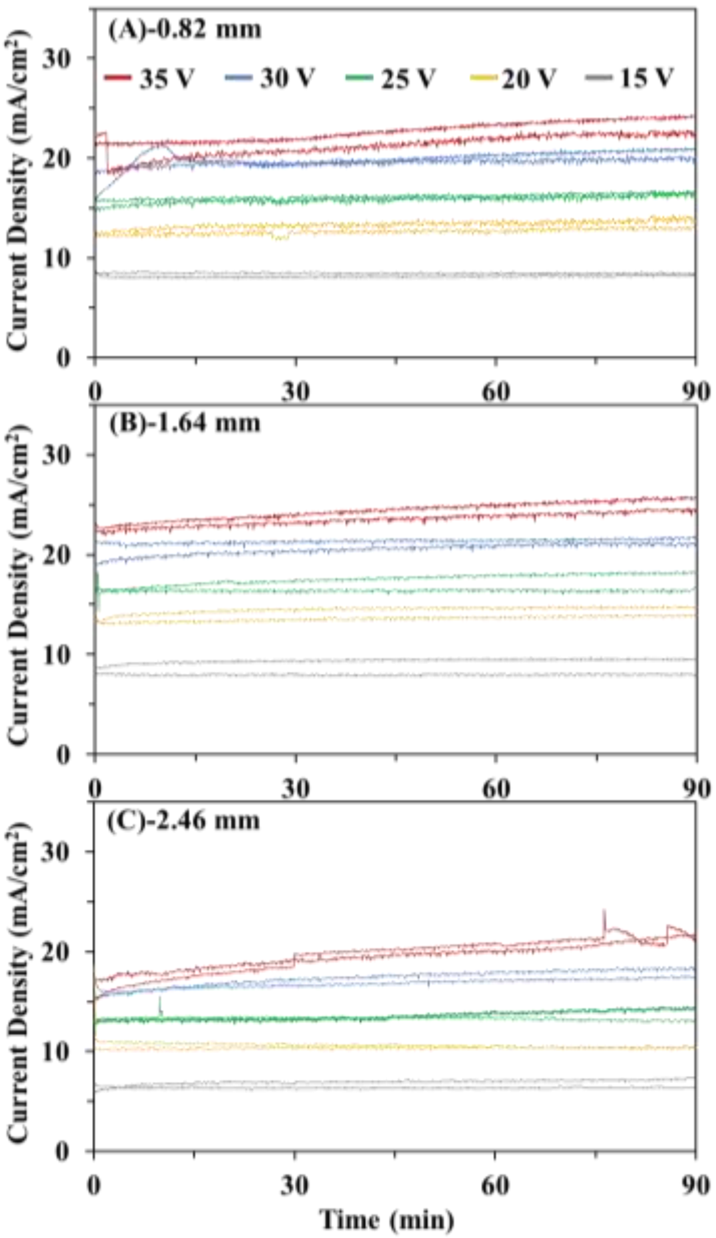

Figure 2.3 Change in current density over time at different voltage applications with (A)-0.82, (B)-1.64, and 2.46 mm inter-membrane distance series

while the current decreased by 15-22% for 2.46 mm series relative to 0.82 and 1.64 mm series. The current density of 1.64 mm series increased by 9-29% in comparison to 0.82 and 2.46 mm series. This can be explained by the increase in volume of the flow inside the feed channels facilitating greater mass transfer at high flow rates (Guo et al., 2021; Kim et al., 2011; Walker et al., 2014). Further, high conductivity in the feed reservoir (Figure S2) augmented the total current density of the BMED stack. Current density values for 0.82 mm series were very close to 1.64 mm series due to high conductivity of the feed reservoir and absence of additional resistance created by the spacers in 0.82 mm series. The experiments with 2.46 mm inter-membrane distance showed the lowest current density (Figure 2.4) due to stack resistance dominating the total current produced as the spacer thickness was increased by three folds (Kim et al., 2011). Tripling of flow rate inside the feed channels (to maintain constant linear velocity) could not overcome the additional spacer resistance of the membrane stack.

Current density in a single voltage application experiment did not fluctuate much (Figure 2.4) as there was no significant variation in the overall conductivity. The drop in feed conductivity was balanced by the rise in base conductivity. The conductivity in the base chamber was not substantially high (Figure S1). This can be justified with the high pH (>9) (Figure S2) in the base reservoir since the beginning of experiments. The pH in the base reservoir was greater than the acid dissociation constant (Pk_a-9.4) of ammonia (Freney et al., 1981). As a result, some of the ammonia transferred to the feed reservoir was in its gaseous state (as NH_3) which was not contributive to the conductivity of the base reservoir. Therefore, the current density was not greatly improved with the conductivity in the base reservoir. However, high current densities were obtained with 0.82, 1.64, and 2.46 mm series in comparison to previous studies (Guo et al., 2021; Mohammadi et al., 2021). Moreover, the maximum electric current density in the BMED operation did not surpass the maximum allowable electric current density (32.5 mA/cm^2) of the BPMs. Thus, the performance of the BMED process was not limited by the BPMs (Aritomi et al., 1996; Krol et al., 1998).

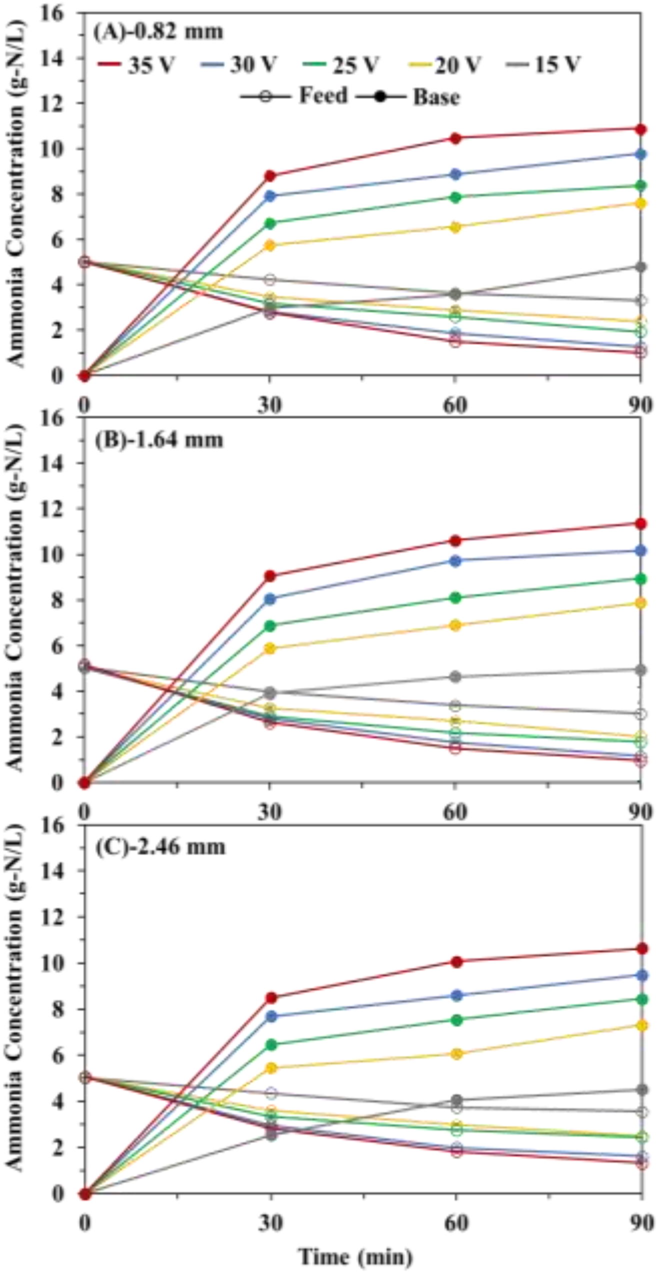

Figure 2.4 Change in ammonia concentration of feed and base reservoirs over time at different voltage applications (A)-0.82, (B)-1.64, and 2.46 mm inter-membrane distance series

2.3.1 Effect of applied voltage on ammonia recovery

The highest ammonia recovery (81%) was achieved at 35 V application in 1.64 mm series (Figure 2.5). The doubling up of flow rate inside the feed channels in 1.64 mm series led to high current densities accelerating mass transfer across the membranes (Guo et al., 2021; Kim et al., 2011; Walker et al., 2014). 80-74% ammonia recovery efficiencies were obtained for 0.82 and 2.46 mm series respectively at 35 V. A negligible loss (1%) in recovery efficiency was observed in 0.82 mm series in comparison to 1.64 mm series at 35 V. At 30 V, 0.82 mm showed an ammonia recovery efficiency of 75% while 1.64 mm series showed a recovery percentage of 77. The percentage loss in recovery efficiency at 30 V in comparison to 35 V for 0.82 and 1.64 mm series was 5-4% respectively. Therefore, 0.82 and 1.64 mm inter-membrane distances work best for ammonia recovery at the voltage applications of 30 and 35 V.

The lowest ammonia recovery was obtained in 2.46 mm series due to comparatively low current densities at different voltage applications. However, a significant loss of ammonia recovery was not observed with 2.46 mm series in comparison to 0.82 and 1.64 mm series. The percentage difference of ammonia loss in 2.46 mm series relative to 0.82 and 1.64 mm series was 6-7% at 30 V and 7-9% at 35 V. Further, the recovery efficiency of ammonia increased with the applied voltage from 15 to 35 V (Figure 2.5) in all three series.

The ammonia concentration factor at the beginning of the experiments of the three series ranged in between 3.5-3.7 which decreased gradually to 2.8-3.0 due to slow recovery of ammonia in the latter stage of the experiments. Formation of concentration gradients with time greatly influenced slow ammonia recovery (decline in slope-Figure 2.5)(Guo et al., 2021). The base reservoir was not capable of reaching the maximum ammonia concentration due to volatilization of ammonia to the atmosphere. For instance, a concentration of 16.82 g-N/L should be gained at the end of 90 minutes for 35 V application in 1.64 mm inter-membrane distance series. However, the final concentration obtained was 11.37 g-N/L. The loss of 5.45 g-N/L was accounted for ammonia loss to the atmosphere. The noticeably high pH (>10) (Figure S1) at the end of the experiments in the base reservoir caused more ammonia to exist in its gaseous form, not in its ionic form as NH_4^+. This could also be proved by the intense odor of ammonia gas emitted during the experiments which was very highly concentrated in the base reservoir. Overall, the ammonia loss to the atmosphere is about 15% of the total mass of ammonia introduced to the system. Moreover, the ammonia loss to the electrode rinse reservoir at the end of each experiment was negligible (<1%). Therefore, the loss of ammonia could be explained mostly as volatilization as back-diffusion was minimized (section 2.2.5).

2.3.2 Cation competition on ammonia recovery

1.64 mm series showed the highest cation separation efficiency for all cations at different voltage applications (Figure 2.6). This can be explained with comparatively high current densities in 1.64 mm series as high current densities favor high ion transfer through the membranes. Among the voltages applied, the highest cation separation efficiency was obtained at 35 V for all three experimental series (Figure 2.6). The cation with the highest separation efficiency at 30 and 35 V was found to be K^+ in all three series followed by NH_4^+. Percentage increments of 1.6% and 3.5% were observed with K^+ separation at 35 V in 1.64 mm series with respect to 0.82 and 2.46 mm series. At 15, 20, and 25 V, the separation efficiency of NH_4^+ was dominant over K^+ in all three series which suggests that separation of NH_4^+ was favored at lower voltage applications. The relative decrease in separation efficiency of NH_4^+ at higher voltages is influenced by very high ammonia concentration in the base reservoir at higher voltages since sharp concentration gradients are formed between the feed and base reservoirs (Guo et al., 2021). Moreover, K^+ possesses the second highest equivalent ionic conductivity (0.007350 m^2 S mol^{-1}) among all the cations (while NH_4^+ shows the highest (0.007348 m^2 S mol^{-1})) which also influenced the rate of separation at higher voltages.

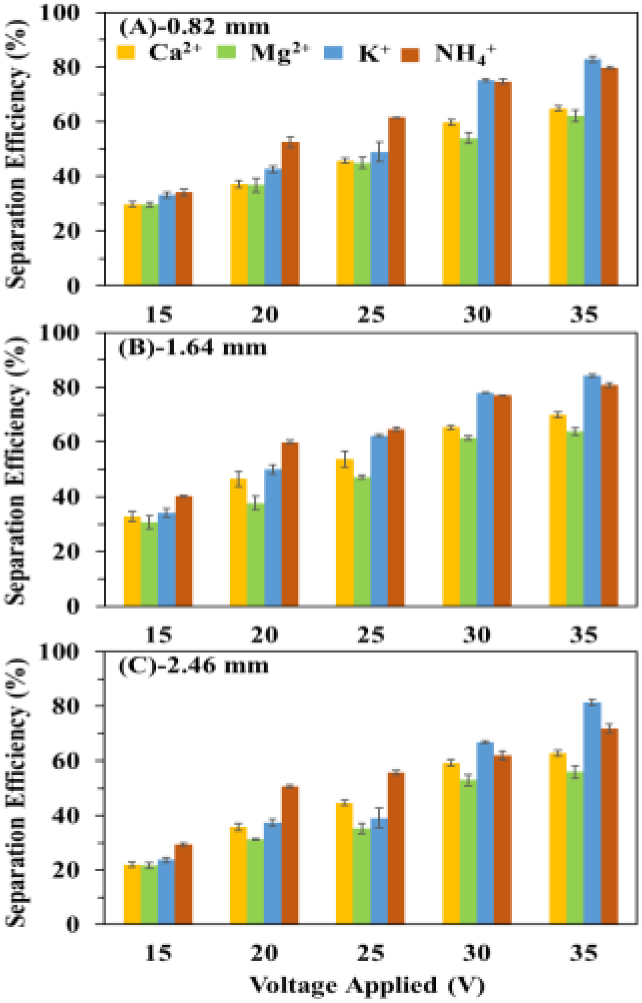

Figure 2.5 Separation efficiency of cations at different voltage applications with (A)-0.82, (B)-1.64, and 2.46 mm inter-membrane distance series

Both Mg^{2+} (0.0053 m^2 S mol^{-1}) and Ca^{2+}(0.005947 m^2 S mol^{-1}) have approximately similar ionic conductivities, therefore, their separation efficiencies were similar. The separation efficiency of Na^+ was not considered in this study as the feed reservoir received sodium ions from the electrode rinse reservoir.

2.3.3 Scaling in BMED

$Ca^{2+}$and Mg^{2+} are the two main ions which could pose scaling risks in this study. It should be noted that the residual amounts of $Ca^{2+}$and Mg^{2+} in the base reservoir were substantially low (<2%) in this study indicating that regular CIP procedure was effective in controlling scale formation in BMED (Figure 2.7). The residual concentrations of $Ca^{2+}$and Mg^{2+} in the base reservoir were high in comparison to the feed reservoir. This can be explained by concentration polarization on the base side due to steep concentration gradients which promote the deposition of $Ca^{2+}$and Mg^{2+} precipitates on the membrane surface at the base side

(Strathman, 2004). The concentration gradients formed are even steeper with higher current densities (30 and 35 V) resulting in higher amounts of precipitates with high voltage applications. Further, the generation of OH^- ions due to water splitting at bipolar membrane junction was greatly induced at high voltage applications promoting deposition of hydroxides of $Ca^{2+}$and Mg^{2+}(Guo et al., 2022). In a previous study conducted by Guo et al. (2020) with dewatering centrate, they observed greater amounts of precipitation ranging 48-59% of Ca^{2+} and 36-43% of Mg^{2+} in the CIP solutions in comparison to initial mass of in the dewatering centrate. The substantially low precipitation of $Ca^{2+}$and Mg^{2+} in this study was due to CEMs being highly affinitive to NH_4^+ than $Ca^{2+}$and Mg^{2+}. This can be further demonstrated by only a slight drop in conductivity of the feed reservoir (Figure S2) at the end of experiments implying rapid NH_4^+ transfer through the CEMs than $Ca^{2+}$and Mg^{2+} (Mohammadi et al., 2021).

Formation of carbonates of Ca^{2+} and Mg^{2+} is not considered in this study as the pH of the feed reservoir is in neutral range. The feed pH is less than the first acid dissociation of carbonic acid (PK_{a1}) (Figure S1). Therefore, the concentration of CO_3^{2-} to form precipitates in the feed reservoir is negligible. As CEMs used in this study are highly impermeable to anions (transport number 97%),%), formation of carbonates in the base reservoir was not a concern. The formation of Ca^{2+} and Mg^{2+} precipitates can be further explained using the Saturation Index (SI) values. According to the SI values, $CaSO_4$(SI=1.3) and $Mg(OH)_2$ (SI=0.7) were the major precipitates in the base reservoir. $CaSO_4$ contributed more to precipitate formation as its concentration in the base reservoir was comparatively higher than Mg^{2+} (Figure 2.7). A defined trend was not observed with K^+ (Figure 6). K^+ is highly soluble and does not cause scaling problems in BMED operation. It was analyzed for comparison purposes to understand how its concentration varied in comparison to scale forming cations such as Ca^{2+} and Mg^{2+}. High concentration of NH_4^+ ions could be seen in the base reservoir for CIP 1. This was not problematic in our study as phosphates were not introduced to the system. Thus, scale formation as struvite crystals was not a concern.

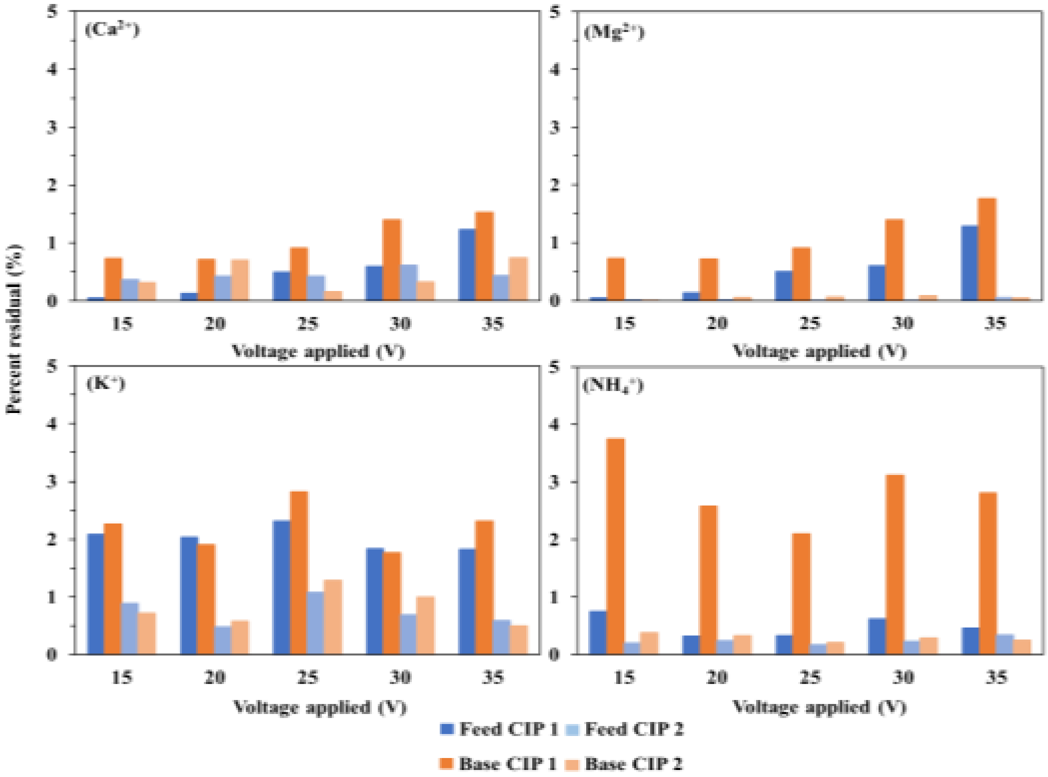

Figure 2.6 Percent residual of cations in feed and base channels found in CIP 1

2.3.4 Control of back-diffusion

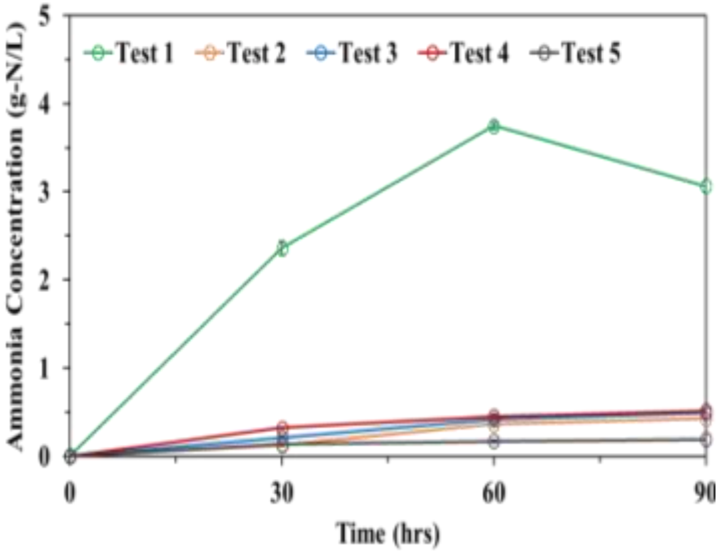

Figure 2.7 Ammonia concentration in the feed side of back-diffusion tests

During voltage application experiments, maintenance of neutral pH in the feed reservoir and alkaline pH in the base reservoir significantly reduced back-diffusion of NH_4^+ (Figure 2.8). Back-diffusion of NH_4^+ was well controlled with both neutral (8.5%) and alkaline pH (9.8%) in the base reservoir while maintaining a neutral pH in the feed reservoir (test 5 and 4). Test 2, with high pH in the base reservoir and neutral pH in the feed reservoir which simulated the final composition of the feed and base reservoirs at the end of voltage application experiments. This indicates that the alkaline pH in the base reservoir during voltage application experiments noticeably minimizes back-diffusion of ammonia to the

feed reservoir as most of the ammonia present is found in its gaseous state (as NH_3).

Back-diffusion is a limitation in BMED application as it affects the recovery of ammonia. High concentration gradient in the BMED system causes considerable back-diffusion of NH_4^+ into the feed reservoir (Rottiers et al., 2014). During voltage application experiments, water splitting in BPM junction provides H^+ to the feed reservoir making feed highly acidic which leads to diffusion of NH_4^+ back to the feed reservoir in exchange of H^+ to the base reservoir. This can be confirmed by the diffusion experiments with low pH in the feed reservoir (Table 2.4-Test 1). A significant back-diffusion of NH_4^+ (84.0%) was observed to the feed reservoir at the end of 90 minutes (Figure 2.8) in test 1 where the feed side was acidic (Table 2.4). Therefore, the optimal pH range in the feed reservoir for prevention of back-diffusion is neutral to slightly basic. The presence of significant amount of bicarbonate (~6000 mg/L) in food liquid digestate helps in maintenance of a neutral pH in the feed reservoir. The H^+ formed in the feed reservoir could be consumed by HCO_3^- in the medium and the bicarbonate buffering action helps in maintaining a neutral pH. Further, it should be noted that the feed pH should not be greater than the second acid dissociation constant of H_2CO_3 (PK_{a2}) as the amount of HCO_3^- left to react with H^+ becomes less (Green et al., 1949). This can also lead to precipitation of salts in the feed reservoir.

Table 2.4 Initial and final pH of feed (F) and base (B) sides of back-diffusion tests

	Test 1		Test 2		Test 3		Test 4		Test 5	
	F	B	F	B	F	B	F	B	F	B
Initial	0.5 ± 0.06	11.7 ± 0.06	7.2 ± 0.02	11.2 ± 0.17	13.4 ± 0.09	11.1 ± 0.12	6.8 ± 0.03	6.7 ± 0.01	6.7 ± 0.06	10.9 ± 0.02
Final	1.4 ± 0.06	1.9 ± 0.16	9.7 ± 0.07	11.8 ± 0.03	13.6 ± 0.06	11.4 ± 0.08	6.4 ± 0.13	6.2 ± 0.13	6.6 ± 0.01	11.2 ± 0.05

2.3.5 Membrane stack energy requirement

The total energy requirement in 0.82, 1.64, and 2.46 mm series varied from 1.24-3.64 kWh/kg-N within 30 minutes, 1.63-5.27 kWh/kg-N within 60 minutes and 2.02-6.94

kWh/kg-N within 90 minutes (Figure 2.9). Rapid ammonia removal during the first 30 minutes led to higher energy efficiency than 60 and 90 minutes (Mohammadi et al., 2021).

The energy requirements of 0.82 and 1.64 mm series at different voltage applications were approximately similar during 30, 60 and 90 minutes operation time (Figure 2.9) due to close current densities (Figure 2.4) and ammonia separation (Figure 2.5). The energy requirement observed at 35 V in all three series was approximately the same. Percentage energy decrements of 18.9-20.7% were observed at 30 V in comparison to 35 V application in 0.82 mm and 1.64 mm series at the end of 90 minutes. Thus 30 V can be considered most suitable for BMED operation in this study due to low energy requirement and high ammonia recovery. The energy requirement of the membrane stack

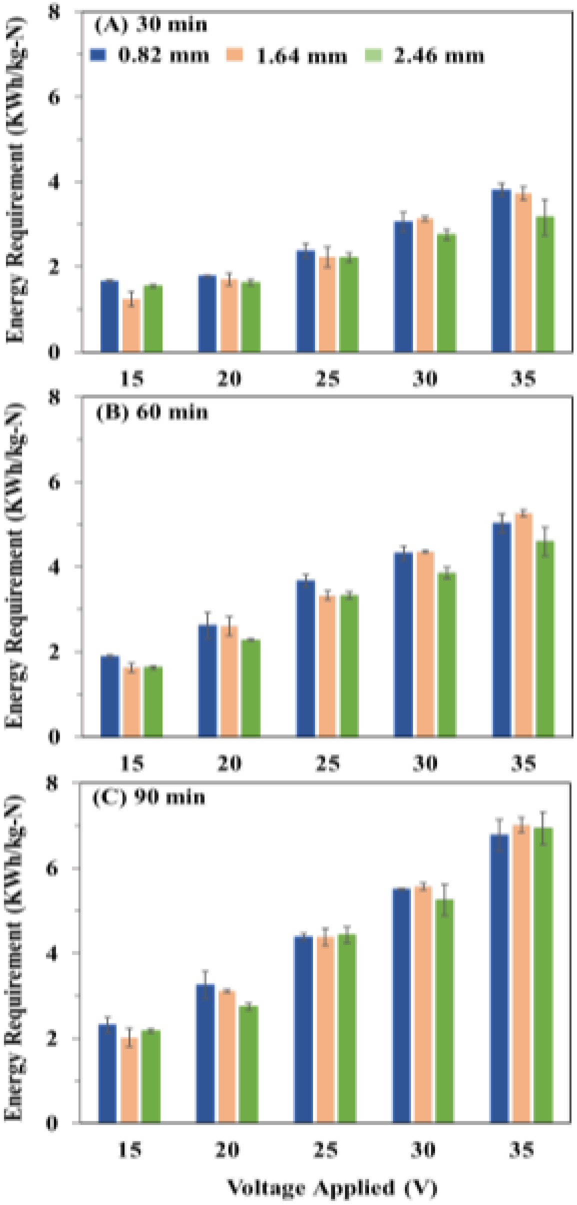

Figure 2.8 Energy requirement of the membrane stack at (A)-30 minutes operation, (B)-60 mins operation, and (C)-90 minutes operation

for an operation period of 90 minutes was comparatively low in comparison to previous studies (Guo et al., 2021; Mohammadi et al., 2021). In previous studies, the average energy requirement for BMED operation in ammonia recovery varied in between 7-16 kWh/kg-N over 60 minutes operation period with an ammonia recovery of 95% (Mohammadi et al., 2021). An energy requirement of 9.6 -24.2 kW h/kg-N over 90 minutes with an ammonia recovery of 70% was obtained by Guo et al. (2021). A recent study conducted by Guo et al. (2023) obtained an ammonia recovery of 74% with an energy requirement of 8.12-11.9 KWh/Kg-N. Further, a very low energy requirement of 4.5 KWh/Kg-N was achieved by Ben Ali et al. (2004) by employing a bench-scale BMED stack. However, the ammonia recovery was only 50% over an operation period of 120 minutes. Therefore, the energy requirement in our study could be considered relatively low with high ammonia recovery in comparison to previous studies.

A study conducted by Li et al. (2015) using a simulated NH_4Cl showed that the energy requirement of the BMED stack increased at stable current densities when NH_4Cl concentration reached below the “inflection point concentration” due to drastic drop in conductivity of the feed reservoir. In our study, the concentration of ammonium chloride in feed reservoir went below 8000 mg/L during 60 to 90 minutes operation period for all three experimental series at 30 and 35 V application; for instance, in 2.46 mm series (with the lowest NH_4^+ transfer to the base reservoir), the concentration of ammonium chloride was found around 7603 mg/L and 6992 mg/L at 60 minutes with 30 and 35 V application while 6724 mg/L and 5731 mg/L with 1.64 mm series (with the highest NH_4^+ transfer to the base reservoir). However, the BMED stack was able to sustain low energy requirement throughout the operation period as the conductivity of the feed reservoir was not substantially affected due to high Cl^- and Na^+ concentration in food liquid digestate (Figure S2). Further, Cl^- ions were trapped inside the feed reservoir due to the absence of AEMS in the study.

The energy requirement of the stack was also compared with the Haber Bosch process. Haber Bosch process usually consumes >11 KWh/Kg-N (Razon, 2014; Rouwenhorst et al., 2019) which is high in comparison to the energy requirement of our study. The energy requirement for pumping is negligible as BMED is not considered a pressure driven system as the electrical energy requirement overrides the pumping energy requirement (Strathman, 2004).

2.3.6 Fouling control in BMED

Fouling was not a significant concern in this study due to the absence of soluble COD or large particulate materials in the feed solution. However, the use of AEMs was minimized in this study as there was of no interest in anion separation (except at the cathode terminal) and also to avoid fouling problems as AEMS are more pronged to fouling than CEMs since most of the foulants found in water are negatively charged (Guo et al., 2012).

The stable current densities obtained in the experiments showed that both scaling and fouling problems did not influence the overall performance of the BMED stack.

Conclusion

BMED constituting CEMs and BPMs was investigated for efficient ammonia recovery from simulated food liquid digestate. The AEMs were not used as there was no interest in anion separation and to prevent membrane fouling. Different voltages were applied to recover ammonia by increasing the inter-membrane distance from 0.82, 1.64 and 2.46 mm to identify the optimal inter-membrane distance for efficient recovery of ammonia. The results showed that 0.82 and 1.64 mm inter-membrane distances work best for recovery of ammonia while 1.64 mm inter-membrane distance showed the highest recovery efficiency (81% at 35 V). However, the reduction in ammonia recovery efficiency was not very significant in 2.46 mm series (74% at 35 V). Therefore, the inter-membrane distance could be increased up to 2.46 mm in BMED without a significant loss in recovery efficiency. It was also found that K^+ was separated rapidly than NH_4^+ at higher voltages due to formation of the high concentration gradient through CEMs. The results of scaling tests showed possible deposition of $Mg(OH)_2$ and $CaSO_4$ specifically in base channels, suggesting regular cleaning of the stack was obligatory to minimize scale formation, to enhance the overall performance of the BMED system. The energy requirement for BMED operation was relatively high in contrast to conventional ED systems due to voltage consumption at the BPM junction. A percentage reduction of 18.9-20.7% in energy requirement was found with 30 V in comparison to 35 V with 0.82 and 1.64 mm series. Thus 30 V can be considered as the best voltage for BMED operation with high ammonia recovery efficiency. Further, BMED technology requires low energy with rapid ammonia recovery in comparison to traditional ammonia production processes such as Haber Bosch. Therefore, efficient separation of NH_4^+ from high strength wastewater can be achieved using BMED technology which helps in reducing the nitrogen load into the environment while meeting the nitrogen demand of various industries.

Acknowledgement

This study was funded by Natural Sciences and Engineering Research Council of Canada ((Discovery Grants, RGPIN-2019-06747 & Discovery Accelerator Supplement, RGPAS-2019-00102), and Ontario Ministry of Research and Innovation (Ontario Research Fund-Research Excellence, RE09-077) The authors thank Ms. Monica Han for her support in analytical equipment operation.

Conflict of Interest

The authors declare no conflict of interest.

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Supplementary Information

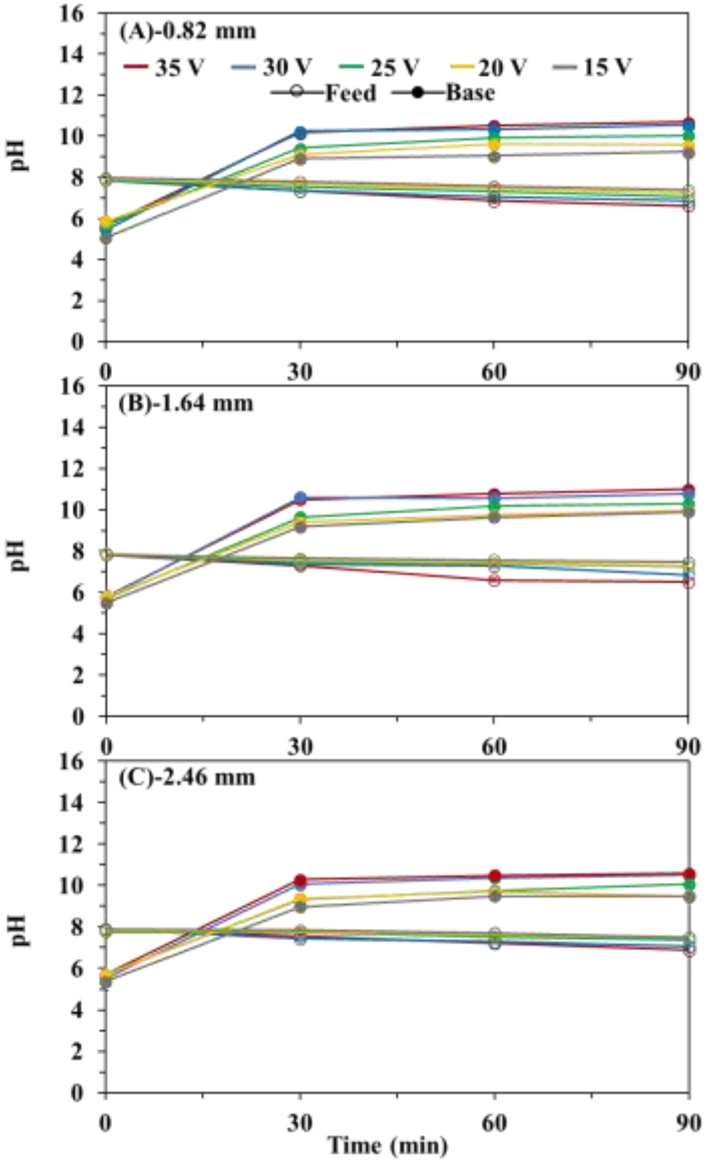

Figure S1 Change in pH of feed and base reservoirs over time at different voltage applications with (A) 0.82, (B) 1.64, and (C) 2.46 mm inter-membrane distances

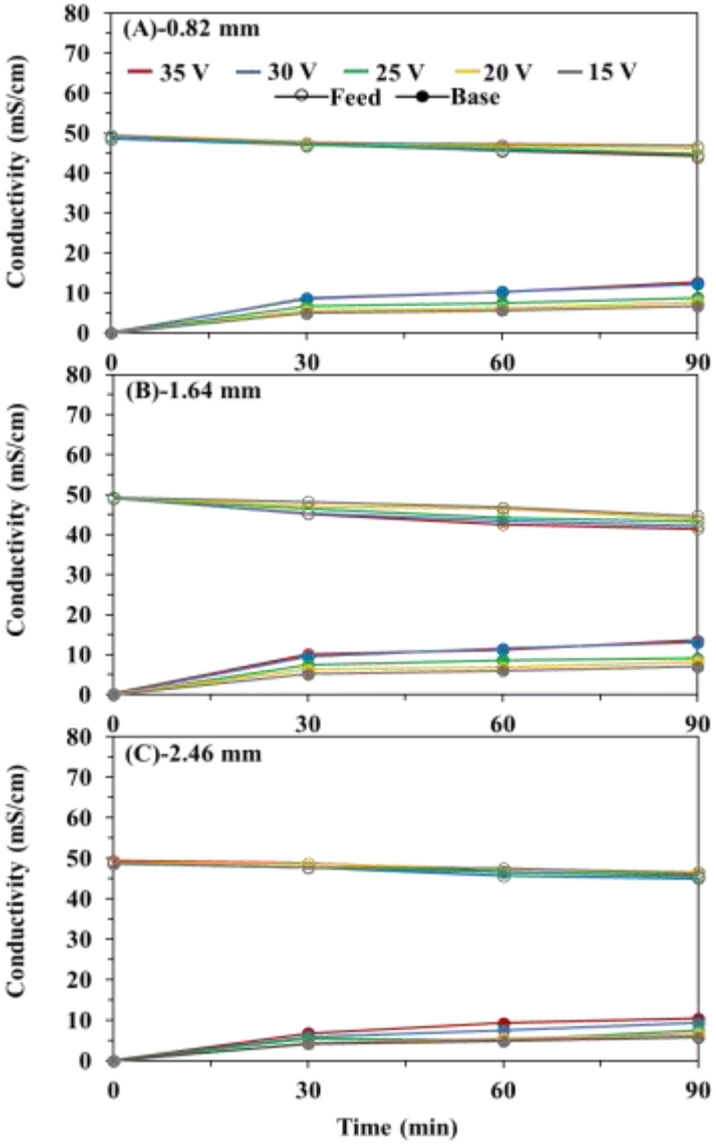

Figure S1 Change in conductivity of feed and base reservoirs over time at different voltage applications with (A) 0.82, (B) 1.64, and (C) 2.46 mm inter-membrane distances

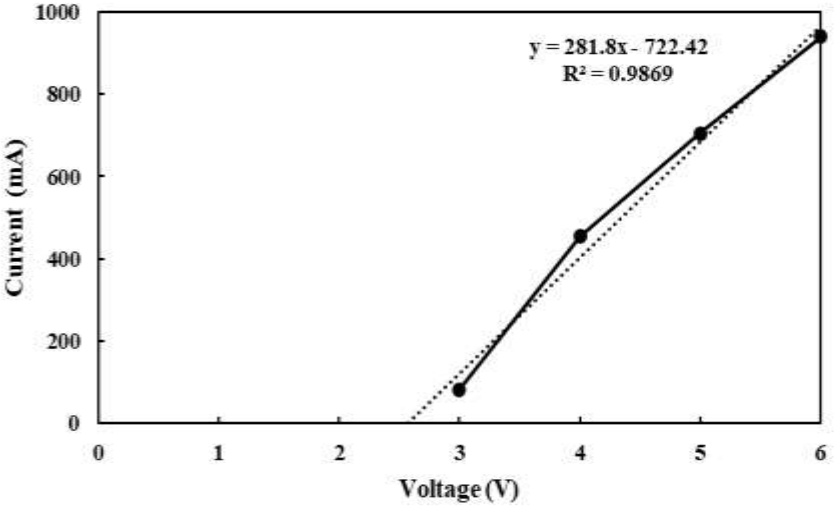

Figure S3 Change of current with voltage for estimation of voltage drop in the electrode rinse cells

Chapter 3. Conclusions and perspectives

3.1 Conclusions

This thesis contains findings, information, and suggestions of operation of a bipolar membrane electrodialysis stack used for recovery of ammonia from simulated food liquid digestate. BMED constituting CEMs and BPMs was investigated for efficient ammonia recovery from simulated food liquid digestate. The AEMs were not used as there was no interest in anion separation and to prevent membrane fouling. Different voltages were applied to recover ammonia by increasing the inter-membrane distance from 0.82, 1.64 and 2.46 mm to identify the optimal inter-membrane distance for efficient recovery of ammonia. The results showed that 0.82 and 1.64 mm inter-membrane distances work best for recovery of ammonia while 1.64 mm inter-membrane distance showed the highest recovery efficiency (81% at 35 V). However, the reduction in ammonia recovery efficiency was not very significant in 2.46 mm series (74% at 35 V). Therefore, the inter-membrane distance could be increased up to 2.46 mm in BMED without a significant loss in recovery efficiency. It was also found that K^+ was separated rapidly than NH_4^+ at higher voltages due to formation of the high concentration gradient through CEMs. The results of scaling tests showed possible deposition of $Mg(OH)_2$ and $CaSO_4$ specifically in base channels, suggesting regular cleaning of the stack was obligatory to minimize scale formation, to enhance the overall performance of the BMED system. The energy requirement for BMED operation was relatively high in contrast to conventional ED systems due to voltage consumption at the BPM junction. A percentage reduction of 18.9-20.7% in energy requirement was found with 30 V in comparison to 35 V with 0.82 and 1.64 mm series.

Thus 30 V can be considered as the best voltage for BMED operation with high ammonia recovery efficiency. Further, BMED technology requires low energy with relatively high ammonia recovery in comparison to traditional ammonia production processes such as Haber Bosch. Therefore, efficient separation of NH_4^+ from high strength wastewater can be achieved using BMED technology which helps in reducing the nitrogen load into the environment while meeting the nitrogen demand of various industries.

3.2 Future directions

This research aimed at optimizing the performance of BMED operation with reference to shortening of operation time and successful scaling control. However, this technology requires employment of practical implementation to treat wastewater commercially. Further, extensive research needs to be carried out in order to recover high purity ammonium hydroxide with no contamination of other cations. New research should be conducted in scaling and fouling control in BMED operation.