AMMONIA SEPARATION USING BIPOLAR MEMBRANE ELECTRODIALYSIS

AMMONIA SEPARATION USING BIPOLAR MEMBRANE ELECTRODIALYSIS IN ANAEROBIC DIGESTION OF ORGANIC WASTE

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Abstract

Nitrogen pollution in the environment creates challenging problems globally and locally and can be effectively controlled by a significant reduction in nitrogen release into the natural water system. In addition, nutrients in high-strength wastewater can be recovered as valuable resources such as different types of ammonium solutions for industrial and agricultural utilizations. Selective ammonia separation from high-strength wastewater can be achieved by bipolar membrane electrodialysis (BMED), a relatively new ion exchange technology. A series of 8 bench-scale BMED experiments with bipolar membranes and cation exchange membranes were performed under various voltage applications. Ammonia in the wastewater was rapidly separated and recovered as a high purity ammonium hydroxide solution. BMED operation for 30 minutes at 5.0 V per cell pair was found to be ideal for high purity ammonium hydroxide production and low electrical energy consumption. Additionally, effective organic fouling control and low energy consumption were achieved. The experiments showed a decrease in the feed pH making it ideal for applications in solid-state anaerobic digestion with leachate recirculation. The application of leachate recirculation in solid-state anaerobic digestion (SSAD) has proven effective for mobilizing nutrients and diluting toxic byproducts to enhance biogas production. The leachate after recirculation contains accumulated ammonia and an increased pH and requires water and chemicals for dilution and pH adjustment prior to recirculation. The data from the experiments were used to construct a numerical model for a hypothetical lab-scale and pilot-scale bipolar membrane electrodialysis and solid-state anaerobic digestion with leachate recirculation (BMED-SSAD) system. A final ammonia concentration of less than 2000 mg-N/L in the reactor was found to be achievable by lab-scale (6 mA/cm^2) and pilot-scale (12 mA/cm^2) BMED-SSAD and low electric energy consumption. The results suggest that BMED is an attractive solution for ammonia separation from high-strength wastewater.

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List of Abbreviations

BMED	Bipolar membrane electrodialysis
CEM	Cation exchange membrane
AEM	Anion exchange membrane
BPM	Bipolar membrane
IEM	Ion exchange membrane
COD	Chemical oxygen demand
CIP	Clean-in-place
SSAD	Solid-state anaerobic digestion
LBR	Leach bed reactor
L/S	Liquid to solid

Preface

Chapter 2 of this thesis consists of a published paper with multiple authors. The following is the citation.

Mohammadi, M., Guo, H., Yuan, P., Pavlovic, V., Barber, J., & Kim, Y. (2021). Ammonia separation from wastewater using bipolar membrane electrodialysis. *Electrochemical Science Advances*, e2000030. https://doi.org/10.1002/elsa.202000030

Table 2.2 and the supplementary figure S2.2 are created from the data provided by Hui Guo. Dr. Younggy Kim was my research supervisor and together with Hui Guo provided insight on the bipolar membrane electrodialysis stack operation. The bipolar membrane electrodialysis stack was constructed by Pengyi Yuan from SUEZ. The stack material was provided by the SUEZ company. Pengyi Yuan, Vladimir Pavlovic and John Barber work in research and development at SUEZ and provided insight on the theoretical and technical aspects of electrodialysis. I conducted the experiments and wrote the manuscript for publication with the help of my research supervisor.

Chapter 3 is an unpublished work. However, the data for the model development is from the experiments mentioned in chapter 2. Therefore, section 3.2 is a repeat of “Materials and Methods” from section 2.1. I developed the model and calculations with the help of my research supervisor.

Chapter 1. Introduction

Nitrogen pollution in the environment is a significant problem that leads to eutrophication and subsequent aquatic biodiversity loss.[1] Algal bloom due to eutrophication can be effectively controlled by a significant reduction in nitrogen release into the natural water system.[2] Therefore, efficient ammonia separation from wastewater is of high interest in the wastewater treatment industry.

Handling nitrogen in wastewater treatment plants is an energy-consuming operation.[3] Conventional municipal wastewater treatment plants direct dewatering centrate (liquid separated from anaerobic digestion sludge) back to the conventional activated sludge system for further treatment.[4] High ammonia concentration can increase the load to the treatment plant and require additional pumping and aeration.[3] Similarly, in food waste treatment plants that perform anaerobic digestion of food waste, leachate (liquid seeping out of the sludge) is recirculated into the reactor.[5] Leachate recirculation in anaerobic digestion results in the mobilization of nutrients and dilution of anaerobic digestion waste byproducts.[5] One of the waste byproducts is ammonia (NH_4^+-N) which increases the pH and is inhibitory to methanogenesis at high concentrations in SSAD.[6] Before recirculation, leachate has to be diluted and the excess high ammonia wastewater needs to be disposed of after further treatment.[5] In both cases of municipal wastewater and food waste treatment facilities, the operation becomes significantly more costly.

Additionally, conventional wastewater treatment plants are not designed to recover nutrients from wastewater although both dewatering centrate and food waste leachate are high in ammonia content.[7] Bipolar membrane electrodialysis (BMED) is an ion exchange technology that can be used for selective ammonia separation and recovery from wastewater.[8] The ion exchange membranes consist of AEMs (anion exchange membranes), CEMs (cation exchange membranes), and BPMs (bipolar membranes) for acid and base production.[9] While BMED stacks are built with AEMs, we only employed CEMs and BPMs, since anion separation is not of interest.[10] We focused on recovering ammonia as ammonium hydroxide solution from dewatering centrate at high separation efficiency and low energy consumption while maintaining the high ammonia purity and low volume ratio between recovered ammonium hydroxide solution (200 mL) and feed wastewater (1000 mL). AEMs are more prone to organic fouling compared to CEMs. When treating high strength wastewater such as dewatering centrate and leachate, the organics can potentially cause serious membrane fouling and decrease separation efficiency as well as membrane lifetime.[11] Therefore, it is important to study and control fouling problems.

Other important factors to consider are the purity of the recovered ammonium hydroxide solution in a 2-cell BMED and the efficiency of ammonia separation at relatively high electric current operation. The electric current in BMED can be limited by mass transport near and in the ion exchange membranes or the rate of water permeation into the BPM interface.[12-13] A series of experiments were performed to study the different factors in the BMED stack under various voltage applications. Subsequently, the data was used to construct a numerical model for a hypothetical BMED-SSAD recirculation system comprised of (1) ammonia separation and recovery using a bipolar membrane electrodialysis stack, and (2) solid-state anaerobic digestion with leachate recirculation.

Therefore, this thesis is focused on (1) the limiting current near CEM and BPM, (2) ion-exchange membrane fouling control, (3) purity of recovered ammonium hydroxide solution, (4) constructing a numerical model for the hypothetical BMED-SSAD model, and (5) electric energy consumption in ammonia separation from both dewatering centrate and leachate using BMED.

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Chapter 2. Ammonia Separation from Wastewater Using Bipolar Membrane Electrodialysis

Abstract

Nitrogen pollution is a serious environmental challenge in natural water and thus selective ammonia separation in wastewater treatment is of great importance to decrease the nitrogen load to natural water systems. Bipolar membrane electrodialysis (BMED) is a relatively new ion exchange membrane technology that can be used for ammonia recovery from wastewater as a beneficial substance. A bench-scale BMED stack with 7 pairs of a bipolar membrane (BPM) and a cation exchange membrane (CEM) was operated under various voltage applications to separate ammonia from dewatering centrate (liquid downstream from dewatering of anaerobically digested wastewater sludge). Ammonia in the wastewater was rapidly separated (up to 87% in 30 minutes) and recovered as ammonium hydroxide solution using the BMED stack. We found that the maximum rate of ammonium separation was governed by the concentration polarization near CEMs rather than water transport into BPMs. In addition, even with the significantly high organic level in dewatering centrate (408 mg/L as total suspended solids), high efficient ammonia separation was maintained over 8 repeated BMED operations without any pretreatment of the feed wastewater, indicating effective organic fouling control with regular chemical cleaning. Furthermore, BMED operation for 30 minutes at 5.0 V per cell pair was found to be ideal for high purity ammonium hydroxide production and low electrical energy consumption. Based on the high separation efficiency and low energy consumption, we

suggest that BMED be further investigated as an attractive option for ammonia separation and recovery from wastewater.

2.1 Introduction

Nitrogen pollution in the environment creates challenging problems globally and locally, such as harmful algal bloom, threatening aquatic ecosystems and even human health.[1] Algal bloom due to eutrophication can be effectively controlled by a significant reduction in nitrogen release into the natural water system.[2] In addition, nutrients in wastewater can be recovered as valuable resources[3] such as different types of ammonium solutions for industrial and agricultural utilizations. However, conventional wastewater treatment plants are not designed to recover nutrients from wastewater although there exist high strength-wastewater streams that can potentially be used for nutrient separation in most domestic wastewater treatment plants.[4-5] The dewatering centrate is a liquid downstream from the dewatering processes of organic waste, such as wastewater sludge, and contains large amounts of ammonia (~1000 mg-N/L).[6] As there are no established technologies for selective ammonia separation from high-strength wastewater, we focused on recovering ammonia as ammonium hydroxide solution from dewatering centrate at high separation efficiency and low energy consumption while maintaining the high ammonia purity and low volume ratio between recovered ammonium hydroxide solution (200 mL) and feed wastewater (1000 mL).

Bipolar membrane electrodialysis (BMED) can be used for the selective separation of ammonium ions from wastewater.[7-10] BMED usually consists of AEMs (anion exchange membranes), CEMs (cation exchange membranes), and BPMs (bipolar membranes) for acid and base production.[11] AEMs and CEMs are used to separate anions and cations, respectively, while BPMs dissociate water into hydrogen and hydroxide ions, allowing acid and base production (e.g., HCl and NaOH). While BMED stacks are built with AEMs, we only employed CEMs and BPMs, since anion separation is not of interest.[12] In previous studies, Li et al. and Lv et al. successfully recovered ammonium from synthetic ammonium chloride solution using BMED.[9-10] However, dewatering centrate has high levels of organics (487 – 800 mg-COD/L);[6] as a result, the organics can potentially cause serious membrane fouling and decrease separation efficiency as well as membrane lifetime.[13-16] Since dewatering centrate or dewatering filtrate is ubiquitous in all modern municipal wastewater treatment facilities, it can be used as model wastewater for studying and controlling fouling problems. Also, to our knowledge, there has been no systematic investigation on the utilization of dewatering centrate in BMED applications.

In ammonium hydroxide production from wastewater using BMED, one important factor for the produced ammonium hydroxide solution is the purity of the recovered solution. Shi et al. demonstrated an increase in the purity of the recovered ammonium solution using BMED while treating pig manure by frequent replacement of the acid and base solutions.[8] In another study, Shi et al. compared the separation rate of individual ions and found higher levels of impurity in the recovered ammonia solution from a synthetic solution using a 3-cell BMED system compared to a 2-cell BMED system.[7] There is still limited understanding of how BMED operation conditions affect the purity of the recovered ammonia solution.

In addition, electric current in BMED can be limited by mass transport near and in the ion exchange membranes.[17] The limiting current near a CEM is triggered by the concentration polarization where the ionic concentration decreases in the diluate boundary layer and eventually reaches zero at the membrane surface, resulting in no further increase in ion transport even at higher applied voltages.[17] The limiting current observed in BPM systems is different and defined by the rate of water permeation into the BPM interface where proton and hydroxyl ions are created from water dissociation under a strong electric field.[18] To our knowledge, it is still not clear whether the maximum rate of ammonium separation is governed by the concentration polarization near CEMs or the water permeation into BPMs in BMED operation. Therefore, this paper is focused on (1) the limiting current near CEM and BPM, (2) IEM fouling control, (3) purity of recovered ammonium hydroxide solution, and (4) electric energy consumption in ammonia separation from dewatering centrate using BMED.

2.2 Materials and Methods

2.2.1 BMED reactor construction and operation

A lab-scale BMED stack was prepared using 7 pairs of CEMs (CR67, SUEZ Water Technologies & Solutions, Canada) and BPMs (AR103 and CR61, SUEZ Water Technologies & Solutions, Canada) for batch operation (Figure 2.1). Polyethylene mesh spacers (1 mm of thickness) were placed between each membrane, creating an effective IEM area of 36.7 cm^2. The electrodes were titanium plates coated with platinum. One extra CEM (CR67, SUEZ Water Technologies & Solutions, Canada) was placed next to the anode to avoid anions transport into the anode chamber. Similarly, an AEM (AR 204, SUEZ Water Technologies & Solutions, Canada) was placed next to the cathode to prevent ammonium (NH_4^+) loss from the feed cell to the cathode chamber. The physical and chemical characteristics of the IEMs are summarized in Table 2.1.

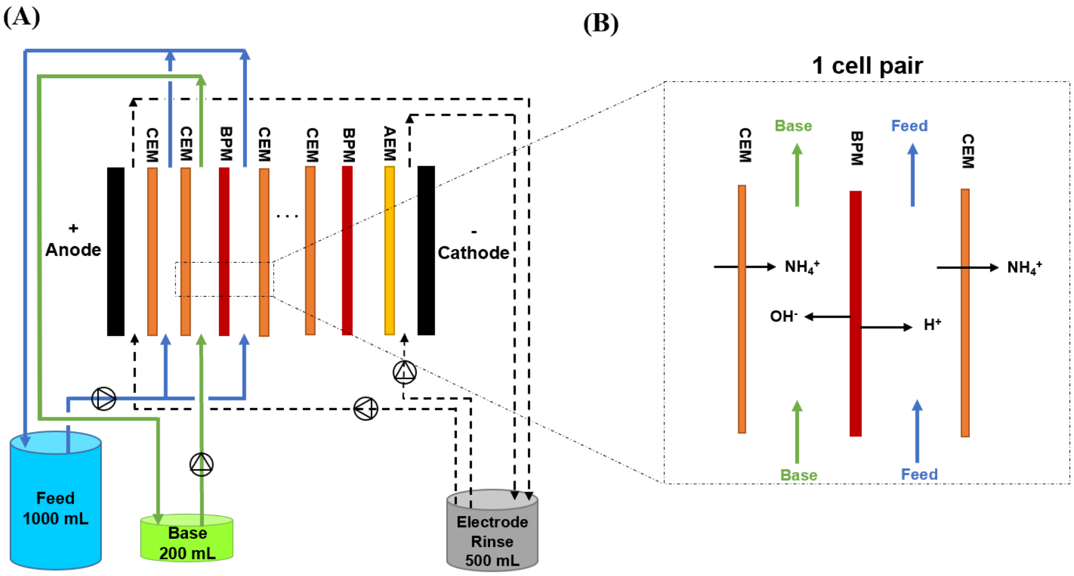

Figure 2.1 (A) Schematic representation of BMED stack set-up used in the experiments. (B) Ion migrations in the BMED system.

Table 2.1. IEM characteristics (provided by the manufacturer)

	AR204	CR67	BPM
Thickness (mm)	0.5	0.6	1.1
Burst strength (kPa)	1034.2	1034.2	>2206.3
Ion-exchange capacity (meq/dry gram membrane)	≥ 2.4	≥ 2.1	-
Resistivity[a] (Ω-cm^2)	7.0	10.0	-
Transport number[b]	82%	95%	-
pH operation range	<10	1-14	1-14

[a] Resistivity in 10 mM NaCl.
[b] Transport number at 0.5 N NaCl: 1 N NaCl.

The anode and cathode were connected to an external power supply box (Model 9201, BK Precision, USA) for electric operation. The electric current was measured and recorded using a digital multimeter system every 20 seconds (34970A, Agilent Technologies, USA). The feed, base, and electrode rinse streams were pumped by 3 peristaltic pumps (Masterflex L/S, Cole-Parmer, Canada). The flow rate of the electrode rinse was 90 mL/min (i.e., 4.9 cm/s in linear velocity) while the feed and base flow rates were 180 mL/min (1.4 cm/s in linear velocity).

Dewatering centrate (liquid separated from anaerobically digested sludge as summarized in Table 2.2) was collected from the local wastewater treatment plant and used as the feed solution (1000 mL). Deionized water (200 mL) was used as the base solution in order to recover high purity ammonium hydroxide solution using the BMED stack. It should be noted that the base conductivity rapidly increased and thus did not limit the generation of electric current in the BMED stack (Figure S1.1A). The electrode rinse solution was prepared with 0.1 M Na_2SO_4 (500 mL). During the operation, the BMED stack was operating in a continuous-recycle mode for 1 hour. The temperature of the feed and base reservoirs was an average of 19.4 ± 0.9℃ at time 0 minutes and an average of 22.3 ± 0.8℃ at time 30 minutes (Orion Versa Star, Thermo Scientific, USA) throughout the experiment. The active water-splitting reaction at BPMs is considered to cause the increase in temperature as previously reported.[19] The BMED stack was set to run for approximately 5 minutes without applied power in order to remove the air bubbles before each experiment. All experiments were performed with the same conditions with varying applied voltage at 2.3, 3.7, 5.0, and 6.4 V per cell pair in duplicates. It should be noted that the minimum voltage for water dissociation in BPMs is approximately 1 V. Thus, the examined cell pair voltages are relatively higher compared to conventional ED operation.

Table 2.2 Dewatering centrate characteristics (n = 4)

Component	Average ± standard variation
Ammonia	1188.85 ± 31.50 mg-N/L
Calcium	120.66 ± 3.46 mg/L
Magnesium	81.66 ± 2.42 mg/L
Potassium	101.58 ± 4.24 mg/L
Sodium	275.21 ± 7.66 mg/L
Soluble COD	457.0 ± 29.0 mg-O_2/L
Screened TSS	408.0 ± 39.0 mg/L
pH	7.63 ± 0.08
Conductivity	10.38 ± 0.05 mS/cm

2.2.2 Cleaning-in-place procedure

After each experiment, a cleaning-in-place (CIP) procedure was conducted with 5% NaCl (1.5 L) and 5% HCl (1.5 L) for 1 h to avoid membrane scaling and organic fouling problems. The flow direction was changed every 30 min. Deionized water (4 L) was used to rinse the BMED stack before and after the CIP process.

2.2.3 Electrode power consumption

A continuous-recycle experiment was conducted with the stack containing the electrodes, 1 CEM, and 1 AEM. Dewatering centrate was used in the feed reservoir when Na_2SO_4 solution was used in the electrode rinse reservoir. The applied voltage was increased every 36 minutes and the current produced was recorded every 10 seconds. Results are presented in Figure S1.2.

2.2.4 Data Collection and Analysis

The volume of each solution was measured at the beginning and end of the experiments. Samples from the base and the feed reservoirs were collected at 0, 30, and 60 minutes. The ammonia concentrations of samples were analyzed using ammonia test kits (Method 10205, Hach Company, USA). The pH and conductivity of the samples were measured and recorded (Orion Versa Star, Thermo Scientific, USA). The ammonia loss from the feed reservoir to the electrode rinse reservoir was lower than 1.4% and hence, considered negligible.

The normalized ammonia concentration (average of duplicates results) was calculated using the ratio of ammonia concentration in feed at times 0, 30, and 60 minutes over the initial ammonia concentration in the feed. The current density was calculated by normalizing current (A) by the membrane effective area of 36.7 cm^2. Energy consumption (kWh/kg-N) was calculated using Eq. (2.1).

$$\text{Energy consumption} = \frac{\Sigma E_{ap} I_t \Delta t}{3600 \times (C_{F(0)} V_{F(0)} - C_{F(t)} V_{F(t)})} \tag{2.1}$$

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

2.3 Results and Discussion

2.3.1 Limiting current in CEM-BPM stacked systems

The average current density increased linearly with increasing applied voltage up to 5.0 V per cell pair (Figure 2.2A). However, above 5.0 V per cell pair (i.e. at 6.4 V per cell pair of the applied voltage), there was no significant increase in the current density suggesting that the BMED stack approached the maximum current density at an average of 14.7 mA/cm^2. The observed maximum current density can be explained by the limiting current in IEM systems. Since the BMED stack consists of CEMs and BPMs, the limiting current can be initiated by the limited ion transport near the cation exchange membranes[17] or slow water permeation into the bipolar membranes.[20]

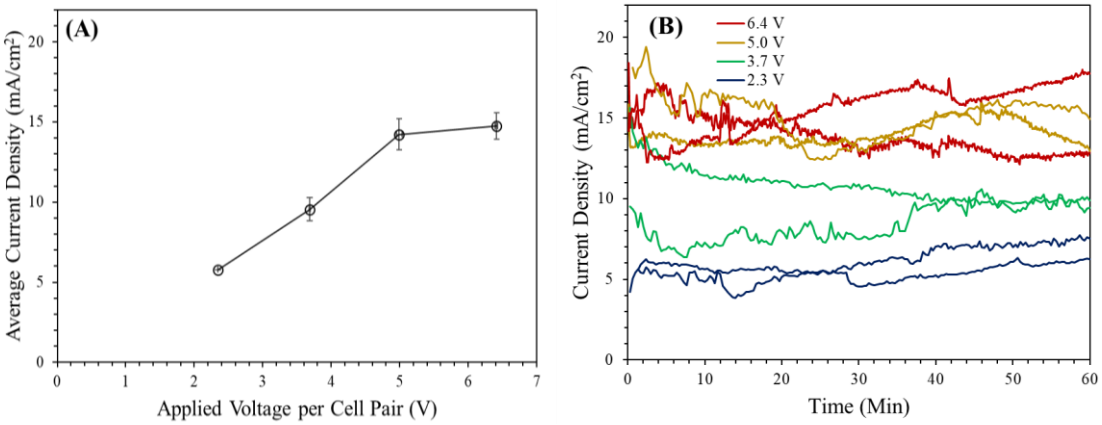

Figure 2.2 (A) Measured average current density throughout the bipolar membrane electrodialysis stack at each applied voltage per cell pair for 4 duplicate experiments. (B) The changes of measured current density (mA/cm^2) throughout the stack over time with different applied voltages.

The limiting current observed in bipolar membrane systems is defined by the rate of water permeation into the BPM interface.[18] For instance, 14.7 mA/cm^2 requires a water permeation flux of 1.5×10^{-7} mol-H_2O/cm^2/s (0.0147 A/cm^2 divided by 96485 C/mol). In a previous study by Aritomi et al. (2001), the limiting current density across a single BPM required a water permeation flux of 1.5×10^{-6} mol-H_2O/cm^2/s (maximum current density of 150 mA/ cm^2)[20], indicating that our observed limiting current density (14.7 mA/cm^2 in Figure 2.2A) cannot be explained by slow water permeation into the BPMs because higher current than 14.7 mA/cm^2 is feasible in the BPM for water splitting into H^+ and OH^-. On the other hand, the magnitude of limiting current density (i_{lim}) near the CEM can be estimated using Eq. (2.2) for mono-valent binary electrolyte solutions.[21]

$$i_{lim} = \frac{FDzC}{t\delta} \tag{2.2}$$

F is the Faraday constant, D is the diffusivity, C is the molar concentration, t is the transport number, and δ is the boundary layer thickness. For example, the limiting current density near a CEM for 78 mM NaCl solution can be calculated as 10 to 20 mA/cm^2 ($D_{Na} = 1.24 \text{ x } 10^{-9}$ m^2/s [17], C = 78 mM , t = 0.95 (Table 1.1), δ = 50-100 µm[17]). Considering that the conductivity of 78 mM NaCl solution (7 mS/cm) is similar to that of the dewatering centrate (Table 2.2), the limiting current density for the CEM and dewatering centrate can be approximated to be 10 to 20 mA/cm^2 assuming the boundary layer thickness ranges from 50-100 µm. Thus, the concentration polarization in the feed-side (i.e., diluate side) boundary layer near CEMs was found to limit the overall separation rate in the BMED stack. It should be noted that this finding on the rate-limitedness by the boundary layer near

CEMs is mainly due to the relatively low ionic content and the low conductivity of the dewatering centrate (7 mS/cm); that is, BMED operation can also be limited by the rate of water permeation into the BPMs for highly saline electrolytes.[18]

2.3.2 Absence of AEMs and fouling control

A relatively constant current density was observed for each of the 60-minute experiments (Figure 2.2B), indicating that organic fouling problems did not limit the ammonia separation even with the substantially high particulate organics in the feed dewatering centrate (screened TSS in Table 2.2). AEMs were not used in the BMED stack in an attempt to reduce fouling effects on electrodialysis performance. Literature reports reveal that an AEM is subject to a greater extent of reversible and irreversible organic fouling compared to a CEM, as most organic foulants in the wastewater effluents are negatively charged.[15, 22] Since anions are not being separated in these experiments, there is no benefit in using AEMs thus avoiding potential organic fouling problems. In addition, a CIP following each experiment was performed in order to reduce the accumulation of organic foulants on the CEMs and scale from the BPM. The conductivity in the base solution increased in the first 30 minutes and remained relatively constant thereafter (Figure S1.1A); hence, the resistance of the ED stack can be considered to be stable except for the starting period of the experiment. The relatively stable BMED stack resistance suggested that the cleaning-in-place methods were effective in reducing the effects of organic and inorganic fouling and no noticeable decrease in electrodialysis performance was observed after a total of 30 hours of BMED operation.

2.3.3 Effect of applied voltage on the ammonia separation efficiency

For 5.0 V per cell pair, 87% of ammonia in the feed reservoir was separated in 30 minutes while 95% removal was achieved after 60 minutes of BMED operation (Figure 2.3). This observation indicates that ammonia was separated rapidly in the first 30 minutes and the separation rate dropped significantly in the following 30 minutes (only 8%). Up to 5.0 V per cell pair, the increased applied voltage resulted in the increased rate of ammonia separation. However, the 6.4 V voltage application per cell pair (i.e., higher than 5.0 V per cell pair) did not enhance the rate of ammonia separation, resulting in only 70% separation in 30 minutes and 91% separation in 60 minutes. This limited (and even reduced) rate of ammonia separation can be explained by the limiting current density above 5.0 V per cell pair (Figure 2.2). While the rate of ammonia separation was slightly reduced for 6.4 V per cell pair experiments, the current density was similar to that of 5.0 V application per cell pair, suggesting that the selective transport of ammonia was reduced at limiting current conditions. This observation can be explained by potential water splitting at the CEM surface near limiting current; as a result, H^+ transport through the CEM could have slowed down the separation of NH_4^+.

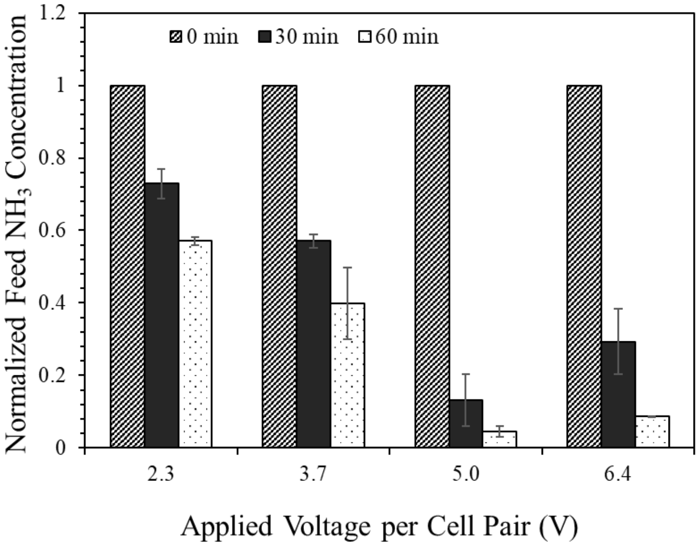

Figure 2.3 The changes in normalized ammonia concentration in the feed reservoir after 30 minutes and 60 minutes for each average applied voltage per cell pair.

For the 5.0 V application per cell pair, the conductivity in the feed reservoir decreased by only 44% in 30 minutes while the ammonia concentration decreased by 87%, indicating that the rate of ammonia separation and selectivity for ammonium ion was higher than the rate of total ion separation in the BMED (Figure 2.4A). The measured conductivity was hardly affected by pH since the feed pH changed from 7.3 to 6.1 in the first 30 minutes (Figure 2.4B); thus, the increased conductivity was contributed by ion separation from the feed to the base cells. A higher rate of ammonia separation compared to the total ion separation rate implies high purity ammonia recovery from wastewater.

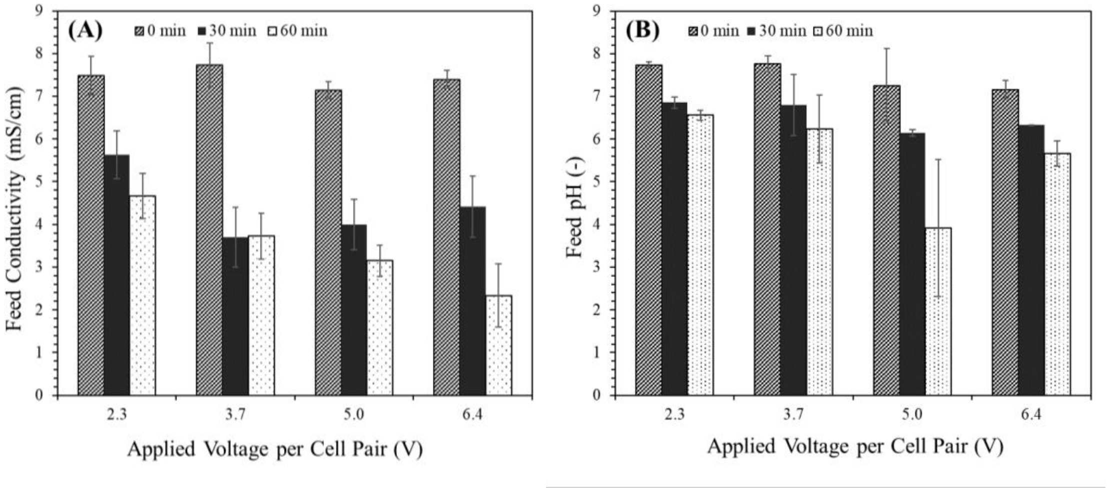

Figure 2.4 The changes in (A) conductivity (mS/cm) and (B) pH in the feed reservoir throughout 4 duplicate experiments.

2.3.4 Water transport

Water transport across CEMs was found to be an average of 20.1 ± 19.6 moles of water per mole of ammonia separation, which is consistent with the previously reported values with NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$[23]. Note that this water transport value was normalized by the amount of ammonia separation while other cations (Table 2.2) also contributed to the amount of water transported through CEMs. For instance, for the 5.0 V application per cell pair, the feed volume decreased from 1000 mL to 981 mL for 60 minutes of operation. This water transport is considered to be driven mostly by electroosmosis as osmotic water transport was presumably minor because the experimental duration was relatively short for 60 min. As a result of the relatively small water transport, the ammonia separation results based on concentration (Figure 2.3) are almost identical to those prepared based on the mass of ammonia separated (Figure S1.3).

2.3.5 Energy consumption of the BMED stack

The electric energy consumption for the BMED stack operation ranged from 7 to 12 kWh/kg-N over the first 30 minutes and 10-16 kWh/kg-N for the 60 minutes operation (Figure 2.5). Energy consumption was found to be in the range of 4.5 to 22 kWh/kg-N reported in previous studies for ammonia separation using BMED.[10, 24-25] The highest energy efficiency in this paper was found for the 5.0 V application per cell pair with 7.7 kWh/kg-N for 87% ammonia separation at 30 minutes. For all the examined conditions, the energy consumption was much lower for the first 30-minute operation since more rapid ammonia separation was achieved compared to the last 30 minutes of BMED operation. A similar electric energy consumption (5 kWh/kg-N) was reported in a recent study by van Linden (2020) where 91% of ammonia was separated (for 60 minutes) from synthetic solution using a lab-scale BMED.[24] They were able to demonstrate the relatively low energy consumption by gradually decreasing the electric current as the degree of ammonia separation increased over the 60-minute operation. Ben Ali et al. (2004) demonstrated a very low energy consumption (4.5 kWh/kg-N) using a lab-scale BMED stack; however, the ammonia separation was only at 50%, indicating incomplete and slow ammonia separation over 2 hours of BMED operation.[25] Operating at 5.0 V per cell pair for 30 minutes proved to be feasible for BMED operation with a relatively high ammonia separation rate and low energy consumption relative to the cited studies.

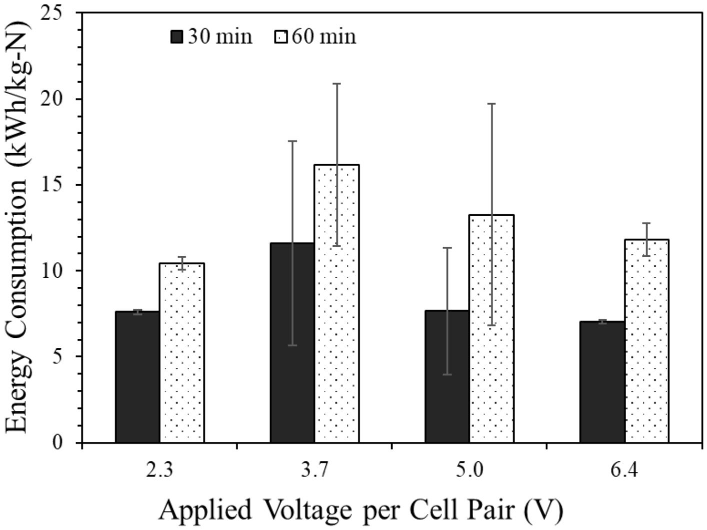

Figure 2.5 The average energy consumption (kWh/kg-N) for 4 duplicate experiments over applied voltage per cell pair (V) after 30 minutes and 60 minutes.

2.4 Conclusions

Different applied voltages were studied to optimize BMED stack operation, increase ammonia separation efficiency, and enhance ammonia recovery. BMED operation at 5.0 V per cell pair resulted in rapid ammonia separation of 87% in 30 minutes with a low energy consumption of 7.7 kWh/kg-N. The recovered ammonia purity was found to be enhanced by reducing the operation time from 60 to 30 minutes. BMED operation near the limiting current density resulted in decreased ammonia selectivity while the energy consumption did not change significantly. Considering ammonia separation rate, purity, and energy consumption, the voltage application of 5.0 V per cell pair for 30 minutes is recommended to operate the BMED. CIP following each experiment was also effective to maintain stable electric current generation and consistent ammonia separation, implying successful organic fouling control on CEMs. Therefore, BMED with CEMs was a feasible method for ammonia separation/recovery with relatively low energy consumption.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

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Supplementary Information

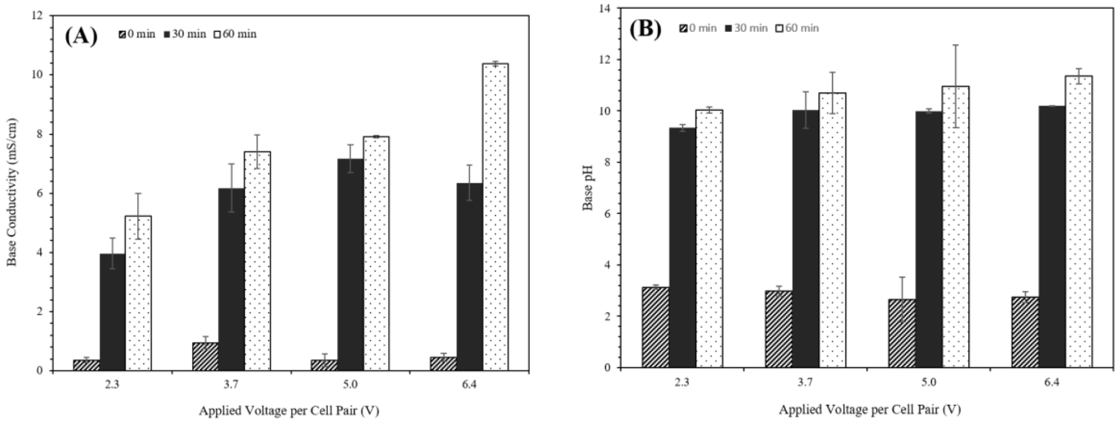

Figure S2.1 The changes in (A) conductivity (mS/cm) and (B) pH in the base reservoir throughout 4 duplicate experiments.

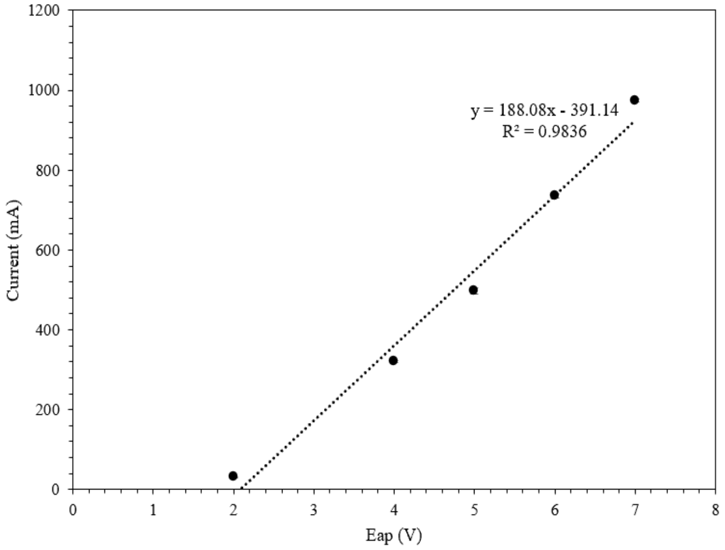

Figure S2.2 Estimation of voltage drop in the electrode rinse cells (including 1 CEM and 1 AEM that encloses the anode rinse cell and cathode rinse cell, respectively). This result was used to calculate the cell pair voltage from the total applied voltage to the electrodialysis stack.

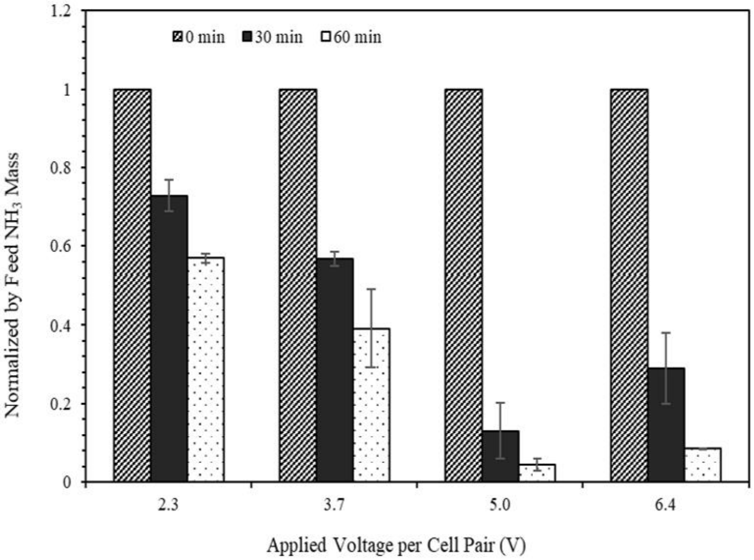

Figure S2.3 The changes in normalized ammonia mass in the feed reservoir after 30 minutes and 60 minutes for each average applied voltage per cell pair.

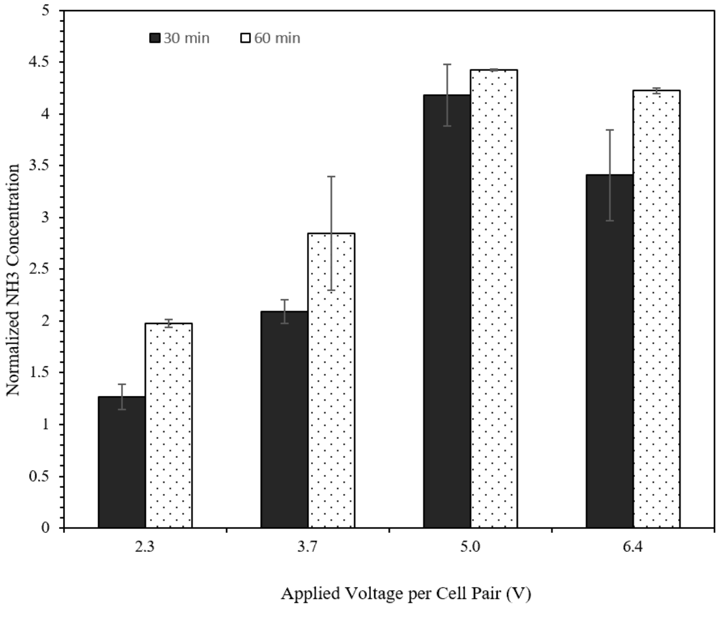

Figure S2.4 The changes in normalized ammonia concentration in the base reservoir after 30 minutes and 60 minutes for each average applied voltage per cell pair.

Chapter 3. Application of bipolar membrane electrodialysis in solid-state anaerobic digestion with leachate recirculation

Abstract

There is an increasing global demand for energy as well as management of food waste landfilling and as a result, energy production from organic waste is a proven and effective solution. Anaerobic digestion of food waste with leachate recirculation is a new technology that has shown great potential for enhanced biogas production. The biggest challenges are the accumulation of ammonia and pH increase in the leachate resulting in the inhibition of anaerobic digestion. Bipolar membrane electrodialysis (BMED) is an effective technology for ammonia separation and recovery. A series of bipolar membrane electrodialysis experiments and a numerical model were performed to propose a bipolar membrane electrodialysis and solid-state anaerobic digestion with leachate recirculation (BMED-SSAD) system. We found that the decrease in the feed pH in the BMED experiments was ideal for applications in leachate treatment prior to recirculation in the anaerobic digestion. In addition, a final ammonia concentration of less than 2000 mg-N/L was found to be achievable by lab-scale (6 mA/cm^2) and pilot-scale (12 mA/cm^2) BMED-SSAD and low electric energy consumption. The results suggest that selective ammonia separation and recovery from leachate with BMED is an attractive solution for enhanced biogas production in solid-state anaerobic digestion of organic waste.

3.1 Introduction

Food waste is associated with 6.8 % of global greenhouse gas emissions and is discharged into landfills.[1] Food waste in landfills produces large amounts of carbon dioxide and methane which result in negative impacts on global warming.[2] One effective strategy in waste diversion from landfills is utilizing food waste in technologies such as anaerobic digestion in order to produce renewable energy (i.e. biogas). Global energy demand is expected to increase by about 30% by the year 2040 and renewable energy production is being encouraged.[3] Therefore, anaerobic digestion of food waste is a simultaneous approach to alleviating the potential energy demand crisis and waste management. Food waste has shown great potential in biogas production due to characteristics such as high volatile solids content, high concentration of organic matter, and a balanced carbon to nitrogen ratio.[4,5] Due to the high total solids concentration of food waste, anaerobic digestion of food waste falls under the category of solid-state anaerobic digestion (SSAD).[6]

The main advantages of SSAD are efficiency and increased organic loading rate which increases methane production.[7] However, the problem with high total solids concentration is that the standard mixing techniques are not feasible and therefore, microorganisms and nutrients are heterogeneously distributed in the biomass and result in suboptimal methane yield.[8] A low-cost, low-maintenance solution is implementing batch mode operation with liquid phase (leachate) recirculation. Leachate recirculation results in the mobilization of nutrients and dilution of anaerobic digestion waste byproducts.[6] One of the waste byproducts is ammonia (NH_4^+-N) which increases the pH and is inhibitory to methanogenesis at high concentrations in SSAD.[9] Ammonium ions in high pH conditions dissociate into free ammonia in the anaerobic digestion reactor (Eq. 3.1).

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \qquad pK_a = 9.3 \qquad (3.1)$$

The hydrophobic free ammonia can diffuse through cell membranes and disrupts the proton and potassium balance resulting in cell inactivation.[10] Therefore, free ammonia has been reported to be inhibitory to microorganisms involved in anaerobic digestion in the range of 53-1450 mg-N/L depending on experimental conditions.[11] Leachate recirculation can be beneficial in the removal of ammonia from the SSAD reactor. However, the leachate needs to be diluted and pH-adjusted prior to recirculation due to the accumulated ammonia which requires additional water and chemical solutions.[6,12–14] As a solution, it is worth considering bipolar membrane electrodialysis.

Bipolar membrane electrodialysis (BMED) is an ion exchange technology that can be used for selective ammonia separation and recovery from wastewater.[15–17] The ion exchange membranes consist of AEMs (anion exchange membranes), CEMs (cation exchange membranes), and BPMs (bipolar membranes) for acid and base production.[18] AEMs and CEMs are used to separate anions and cations, respectively, while BPMs dissociate water into hydrogen and hydroxide ions.[18] While BMED stacks are built with AEMs, we only employed CEMs and BPMs to reduce energy consumption and organic fouling.[19] The absence of AEMs results in the release of H^+ ions into the feed and subsequently, a decrease in feed pH. BMED can be beneficial for ammonia separation and recovery from the leachate before recirculating it back into the SSAD reactor. Food waste has a high concentration of ammonia (7000 - 20000 mg-N/L)[20] and the leachate has shown to accumulate a range of 1000 – 2000 mg-N/L TKN concentration after one day of recirculation.[12] Hence, the high ammonia concentration can be recovered as a high purity solution such as ammonium hydroxide for use in fertilizers without further treatment.[21] Global fertilizer demand is increasing by 3 to 4% a year and current methods of fertilizer production heavily rely on non-renewable energy and finite mineral resources.[22] Therefore, ammonium hydroxide production from anaerobic digestion leachate can be a sustainable solution to help the growing fertilizer demand and ensure food security.

The application of ion exchange membrane technology to anaerobic digestion with leachate recirculation to enhance biogas production has not been studied. Therefore, this paper proposes a BMED-SSAD recirculation system comprised of (1) ammonia separation and recovery using a bipolar membrane electrodialysis stack, and (2) solid-state anaerobic digestion with leachate recirculation. A series of bipolar membrane electrodialysis experiments were conducted to design the BMED component. Subsequently, broad literature reports were reviewed to propose a design for a leach bed reactor (LBR) for the solid-state anaerobic digestion (SSAD). Finally, a numerical model was constructed for the hypothetical BMED-SSAD recirculation system to assess its feasibility and to suggest optimal operating conditions.

3.2 Materials and Methods

A lab-scale BMED stack was prepared using 7 pairs of CEMs (CR67, SUEZ Water Technologies & Solutions, Canada) and BPMs (AR103 and CR61, SUEZ Water Technologies & Solutions, Canada) for batch operation (Figure 3.1). One extra CEM

(CR67, SUEZ Water Technologies & Solutions, Canada) was placed next to the anode and an AEM (AR 204, SUEZ Water Technologies & Solutions, Canada) was placed next to the cathode. The purpose of the extra membranes was to avoid anion transport into the anode chamber and ammonium loss from the feed cell to the cathode chamber. Polyethylene mesh spacers (1 mm of thickness) were placed between each membrane, creating an effective IEM area of 36.7 cm^2. The electrodes were titanium plates coated with platinum. The physical and chemical characteristics of the IEMs are summarized in Table 3.1.

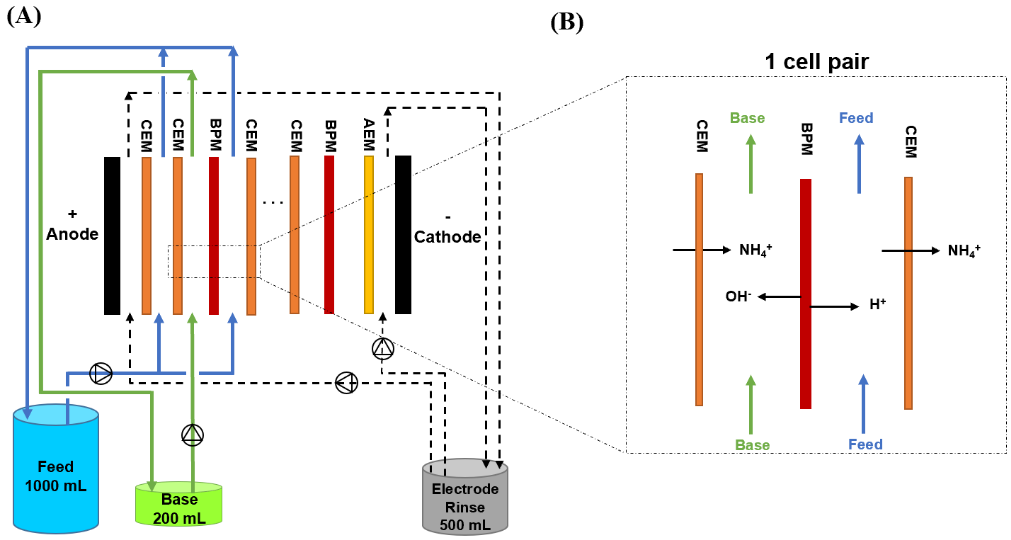

Figure 3.1 (A) Schematic representation of BMED stack set-up used in the experiments. (B) Ion migrations in the BMED system.

Table 3.1 IEM characteristics (provided by the manufacturer).

	AR204	CR67	BPM
Thickness (mm)	0.5	0.6	1.1
Burst strength (kPa)	1034.2	1034.2	>2206.3
Ion-exchange capacity (meq/dry gram membrane)	≥ 2.4	≥ 2.1	-
Resistivity[a] (Ω-cm^2)	7.0	10.0	-
Transport number[b]	82%	95%	-
pH operation range	<10	1-14	1-14

[a] Resistivity in 10 mM NaCl.
[b] Transport number at 0.5 N NaCl: 1 N NaCl.

The anode and cathode were connected to an external power supply box (Model 9201, BK Precision, USA) for electric operation. The electric current was measured and recorded using a digital multimeter system every 20 seconds (34970A, Agilent Technologies, USA). The feed, base, and electrode rinse streams were pumped by 3 peristaltic pumps (Masterflex L/S, Cole-Parmer, Canada). Flow rates of each cell are presented in Table 3.2.

Table 3.2 Operating conditions for the 8 electrodialysis experiments.

Reservoir	**Solution**	**Flow rate (Linear velocity)**
Feed	1000 mL dewatering centrate	180 mL/min (1.4 cm/s)
Base	200 mL deionized water	180 mL/min (1.4 cm/s)
Electrode rinse	500 mL 0.1 M Na_2SO_4	90 mL/min (4.9 cm/s)

Dewatering centrate (liquid separated from anaerobically digested sludge as summarized in Table 3.3) was collected from the local wastewater treatment plant and used as the feed solution. Deionized water was used as the base solution in order to recover high purity ammonium hydroxide solution using the BMED stack. The electrode rinse solution was prepared with 0.1 M Na_2SO_4. The volume of each reservoir is presented in Table 3.2. During the operation, the BMED stack was operating in a continuous-recycle mode for 1 hour. The BMED stack was set to run for approximately 5 minutes without applied power in order to remove the air bubbles before each experiment. All experiments were performed with the same conditions with varying applied voltage at 2.3, 3.7, 5.0, and 6.4 V per cell pair in duplicates.

Table 3.3 Dewatering centrate characteristics (n = 4)

Component	Average ± standard variation
Ammonia	1188.85 ± 31.50 mg-N/L
Calcium	120.66 ± 3.46 mg/L
Magnesium	81.66 ± 2.42 mg/L
Potassium	101.58 ± 4.24 mg/L
Sodium	275.21 ± 7.66 mg/L
Soluble COD	457.0 ± 29.0 mg-O_2/L
Screened TSS	408.0 ± 39.0 mg/L
pH	7.63 ± 0.08
Conductivity	10.38 ± 0.05 mS/cm

All experiments were performed with the same conditions with varying applied voltage at 2.3, 3.7, 5.0, and 6.4 V per cell pair in duplicates. After each experiment, a cleaning-in-place (CIP) procedure was conducted to avoid membrane scaling and organic fouling problems.

Samples from the base and the feed reservoirs were collected at 0, 30, and 60 minutes. The ammonia concentrations of samples were analyzed using ammonia test kits

(Method 10205, Hach Company, USA). The ammonia loss from the feed reservoir to the electrode rinse reservoir was lower than 1.4% and hence, considered negligible. The current density was calculated by normalizing current (A) by the membrane effective area of 36.7 cm^2. Feed reservoir volume was measured at the beginning and the end of the experiment. To simulate continuous flow conditions, only data from the second half of the experiment (30 minutes) were used, allowing sufficient time for stabilization, and reaching near steady-state conditions.

3.3 Model Development

A hypothetical coupled system was designed comprised of a solid-state anaerobic digestion leach bed reactor (LBR) and a BMED stack (BMED-SSAD). The LBR was designed with two compartments as an anaerobic digestion reactor and a leachate collection tank. In the design, a cylindrical tank was proposed to be stacked on top of a second identical tank forming the two compartments. A steel mesh was recommended to be placed between the two compartments to act as a filter for leachate separation. A valve and tube system at the bottom of the reactor would function as an outlet for leachate collection and subsequently, the leachate influent to the BMED stack. The effluent tube of the BMED stack was proposed to be connected to a sprinkler at the top of the anaerobic digestion reactor. The sprinkler would aid in an even distribution of the leachate. A schematic of the proposed hypothetical design is presented in Figure 3.2.

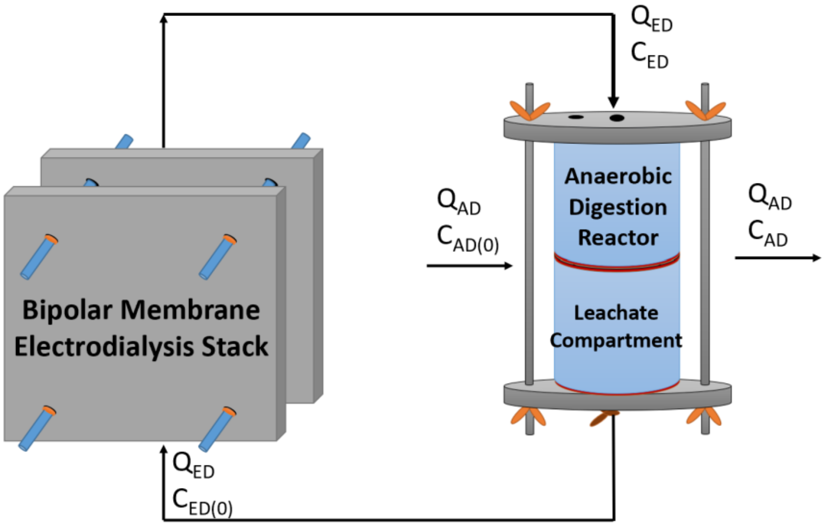

Figure 3.2 Schematic diagram of a hypothetical BMED-SSAD recirculation system

A mathematical model was built to simulate the operation of the BMED-SSAD recirculation system for a hypothetical lab-scale and pilot-scale operation. Figure 3.2 illustrates the mass balance components of the BMED system. Assuming steady-state conditions, the mass balance equation of ammonia can be rewritten as Eq. (3.2).

$$C_{ED} = C_{ED.i} - \frac{R_n E_a}{Q_{ED}} \tag{3.2}$$

$C_{ED,i}$ and C_{ED} represented the ammonia concentration (mg-N/L) in the influent and effluent of the BMED stack, respectively. Q_{ED} represented the flow rate (L/h) of the feed (leachate) into and out of the BMED stack. E_a represented the total effective area (cm^2) of the stack. For example, a stack with 4 cell pairs of 36 cm^2 membrane open area results in an E_a of 144 cm^2 (4 x 36 cm^2 = 144 cm^2). R_n represented the rate of ammonia separation per unit membrane area (mg-N/h/cm^2) in the BMED stack. The operational variable R_n was obtained from our BMED experiments. The rate of ammonia separation per unit membrane area at 180 mL/min flow rate was obtained by using Eq. (3.3) for 8 different values of current density (i).

$$R_n = \frac{(C_{60}V_{60} - C_{30}V_{30})}{256.9\ t} \tag{3.3}$$

R_n represented the rate of ammonia separation per unit membrane area (mg-N/h/cm^2) at a given current density. C_{60} and V_{60} were the feed ammonia concentration and reservoir volume at 60 minutes, respectively. C_{30} and V_{30} were the feed ammonia concentration and reservoir volume at 30 minutes, respectively. The total operation time was denoted as t (0.5 hour) and the total CEM membrane effective area was calculated as 256.9 cm^2 (7 membranes x 36.7 cm^2).

Figure 3.2 illustrates the mass balance components of the anaerobic digestion system. Assuming steady-state conditions and assuming that ammonia was only removed through BMED, the mass balance of ammonia can be rewritten as in Eq. (3.4).

$$C_{AD} = C_{AD,i} + \frac{Q_{ED}}{Q_{AD}} (\Delta C_{ED}) \tag{3.4}$$

$C_{AD,i}$ and C_{AD} represented the initial and final ammonia concentration (mg-N/L) in the anaerobic digestion operation, respectively. Q_{AD} represented the flow rate (L/h) of the anaerobic digestion (HRT divided by the reactor volume). ΔC_{ED} (mg-N/L) was the ammonia concentration difference in the BMED system (C_{ED} – $C_{ED,i}$) obtained from Eq. (3.1).

Energy consumption (kWh/kg-N) was calculated using Eq. (3.5).

$$\text{Energy consumption} = \frac{\Sigma E_{ap} I_t \Delta t}{(C_{AD,i}V - C_{AD}V)} \tag{3.5}$$

E_{ap} (V) was the applied voltage for all of BMED stack (voltage per cell pair multiplied by the number of cell pairs), I (A) was the electric current, and Δt (h) was the time interval (HRT). $C_{AD,i}$ (g/L) and C_{AD} (g/L) were the initial and final ammonia concentrations in the SSAD reactor. V was the volume of the SSAD reactor.

3.4 Results and Discussion

3.4.1 Effect of BMED on feed pH

The pH of the dewatering centrate in the feed reservoir decreased from an average of 7.48 ± 0.27 to an average of 6.53 ± 0.30 pH units after 30 minutes of operation (Figure 3.3). The decrease in pH can be attributed to ammonia separation in addition to the H^+ released into the feed solution from the water-splitting reaction at the bipolar membrane. Due to the buffering capacity in the dewatering centrate, pH remained neutral throughout the experiments. The slight decrease in pH is ideal for applications in SSAD as high pH is inhibitory to anaerobic digestion. In SSAD operation, pH typically increases after multiple leachate recirculations and results in conversion of ammonium to free ammonia.[6] Zeeman et al. (1985) demonstrated that reducing pH from 7.5 to 7.0 during anaerobic digestion increased the methane production by four times.[23] Xu et al. (2011) demonstrated up to an 88% increase in methane production in experiments involving pH-adjusted leachate recirculation.[13] Conventionally, water is added for leachate dilution and chemicals are added for pH adjustment prior to recirculation.[6,12–14] However, the pH of the leachate after BMED would have the desired decrease without the need for dilutions or pH adjustments.

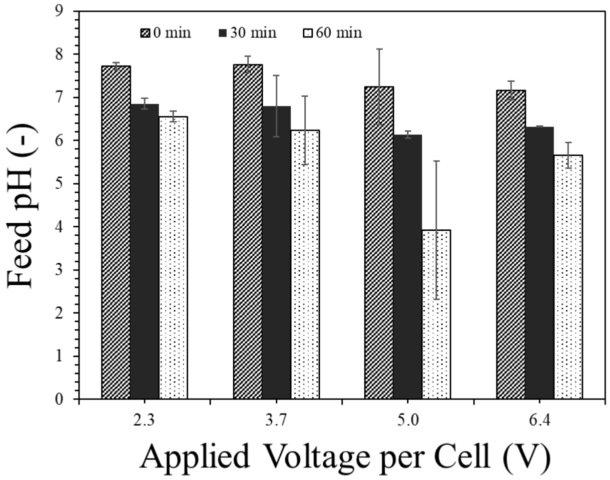

Figure 3.3 The changes in pH in the BMED feed reservoir (n=2).

3.4.2 *Correlation between current density and ammonia separation*

The average current density increased linearly with increasing applied voltage and was correlated with the increasing rate of ammonia separation from the feed solution (Figure 3.4). The measured average current density for 4 duplicate BMED experiments with 1.4 cm/s linear velocity is presented in Figure 3.4A. The minimum voltage per cell pair required for water splitting at the bipolar membranes is 0.86 V.[24] Above 0.86 V per cell pair, an increase in the applied voltage resulted in a linear increase in the measured average current density. The measured current density was then used to graph the correlation between the rate of ammonia separation per unit membrane area and average current density in each experiment for the final 30 minutes (Figure 3.4B).

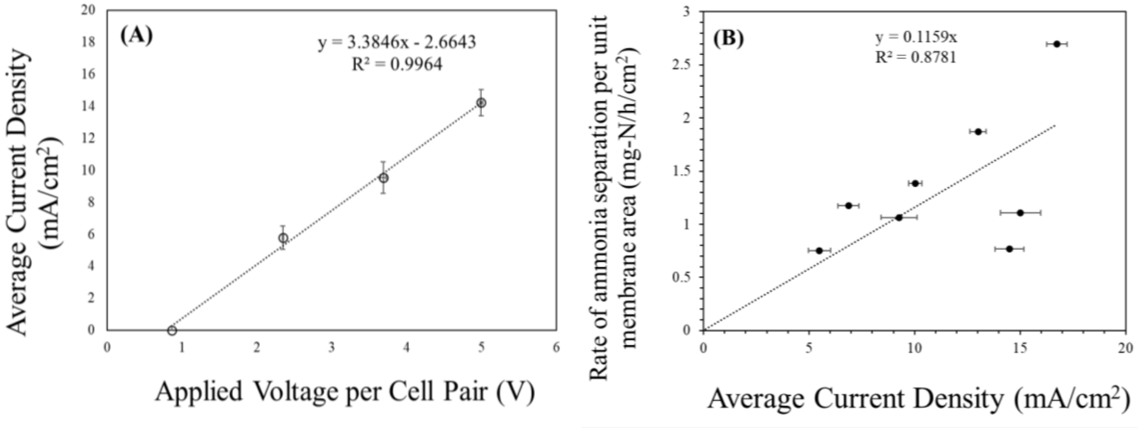

Figure 3.4 (A) Measured average current density throughout the bipolar membrane electrodialysis stack at each applied voltage per cell pair for 4 duplicate experiments. (B) Rate of ammonia separation normalized by unit membrane area (mg-N/h/cm^2) relative to the measured average current density (mA/cm^2) for 8 electrodialysis experiments performed for 30 minutes with a linear velocity of 1.4 cm/s. A linear trendline is presented in each figure.

In the first half of the 1-hour experiments, ammonia was rapidly separated from the feed cell to the base cell initially containing DI water. As a result, the conductivity in the base reservoir rapidly increased from an average of 0.5 ± 0.3 mS/cm (DI water) to 5.9 ± 1.3 mS/cm (ammonium hydroxide) at the beginning of the experiments. Therefore, the second 30 minutes of the experiments were chosen for Figure 3.4B to represent a relatively stabilized condition in the BMED stack. As the average current density increased, the rate of ammonia separation per unit membrane area increased linearly. The linear trendline resulted in the relationship presented in Eq. (3.6).

$$R_n = 0.1159\ i \tag{3.6}$$

R_n (mg-N/h/cm^2) represented the rate of ammonia separation per unit membrane area for a given current density i (mA/cm^2). Subsequently, Eq. (3.4) was used to calculate the rate of ammonia separation per unit membrane area at 3 different values of current density (4, 6, and 8 mA/cm^2 for the lab-scale operation and 10, 12, and 14 mA/cm^2 for the pilot-scale operation) in the BMED-SSAD recirculation system model. The calculated R_n values were then used in Eq. (3.3) to obtain the change in ammonia concentration after the BMED system (ΔC_{ED}).

3.4.3 Example calculations for the lab-scale BMED-SSAD Operation

Our experimental data and a literature review were utilized to perform example calculations to assess the feasibility of the hypothetical lab-scale BMED-SSAD design. The proposed lab-scale BMED-SSAD system was designed to involve a continuous leachate recirculation. Xu et al. (2014) found the optimal leachate recirculation frequency to be continuous to achieve improved food waste hydrolysis.[12] Therefore, a 24-hour continuous electrodialysis operation at a linear velocity of 1.4 cm/s was selected. The linear velocity was kept constant at 1.4 cm/s in order to accurately reflect the rate of ammonia separation R_n obtained from our experiments. A 1:1 liquid to solid (L/S) ratio was selected for the ratio of leachate to solids in the anaerobic digestion reactor. Xu et al. (2014) found the 1:1 L/S ratio selectively enriched hydrolyzing bacteria for enhanced performance.[12] The BMED-SSAD system was designed to operate for 20 days and steady-state conditions were assumed. In the previous study by Xu et al. (2014), it was reported that the TKN concentration in the leachate ranged from 1000 to 2000 mg/L after one day of continuous recirculation.[12] For our hypothetical design, continuous recycle flow of leachate was estimated to result in a leachate ammonia concentration of 1000 mg-N/L flowing into the electrodialysis system as the influent ($C_{ED(0)}$). The ammonia concentration in a 5 L anaerobic digestion reactor with food waste was estimated to be 10,000 mg-N/L ($C_{AD(0)}$).[8,25] It was assumed that ammonia is removed only by the BMED stack in the recirculation system. A summary of the example operating conditions is presented in Table 3.4.

Table 3.4 The proposed lab-scale operating conditions of the BMED-SSAD recirculation system

System	Parameter	Lab Scale	Pilot Scale
Bipolar Membrane Electrodialysis (ED)	$C_{ED,i}$ (mg-N/L)	1000	1000
	Linear Velocity (cm/s)	1.4	1.4
	Membrane open area (cm^2)	36	275
Solid-State Anaerobic Digestion (AD)	HRT (d)	20	20
	Reactor volume (L)	5	10,000
	Q_{AD} (L/h)	0.01	10.4
	$C_{AD,i}$ (mg-N/L)	10,000	10,000

After 20 days of the lab-scale BMED-SSAD operation, the final ammonia concentration in the anaerobic digestion reactor would decrease linearly as the number of cell pairs and current density increased (Figure 3.5). An increase in the current density resulted in a linear increase in the separated ammonia concentration from the leachate (Figure 3.5A). When the leachate after ammonia separation was recirculated back into the SSAD reactor, the final ammonia concentration in the reactor after 20 days would decrease proportionally as the current density increased (Figure 3.5B).

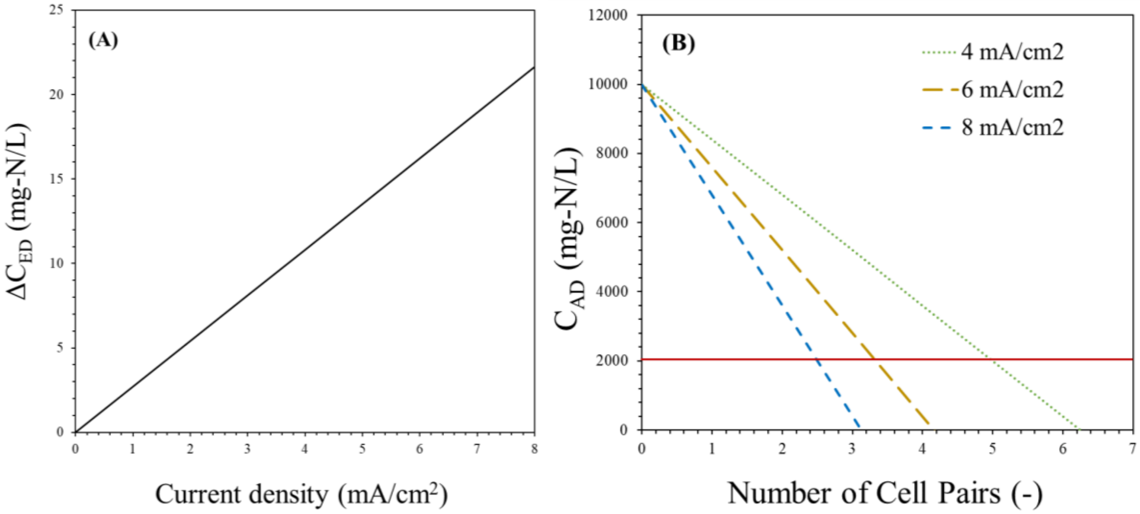

Figure 3.5 Lab-scale BMED-SSAD: (A) The change in the leachate ammonia concentration (mg-N/L) relative to the current density in BMED with 36 cm^2 membrane open area. (B) The final Ammonia concentration in the anaerobic digestion reactor after HRT of 20 days. The red line represents a final ammonia concentration of 2000 mg-N/L.

The final ammonia concentration in the SSAD reactor would decrease proportionally as the number of cell pairs in the BMED increased (Figure 3.5B). For lab-scale operations, it is suggested to operate the BMED stack with 4 cell pairs and 36 cm^2 of membrane open area at 6 mA/cm^2 to achieve a final ammonia concentration of less than 2000 mg-N/L in the anaerobic digestion reactor. Previous studies have reported that the ammonia concentration at a range of 900 – 6000 mg-N/L is inhibitory in anaerobic digestion depending on the type of waste used in the process.[9,10,26] In order to avoid ammonia inhibition, a target SSAD reactor ammonia concentration of 2000 mg/L is suggested represented by a red line in Figure 3.5B. A total ammonia removal should be avoided since ammonia is an essential nutrient for anaerobic microorganisms and is needed at low concentrations.[9,27]

3.4.4 Example calculations for the pilot-scale BMED-SSAD operation

Similar to the previous section, our experimental data and a literature review were utilized to perform example calculations to assess the feasibility of the hypothetical pilot-scale BMED-SSAD design. The proposed pilot-scale BMED-SSAD system was designed to involve a continuous BMED recirculation for 20 days of anaerobic digestion. A 1:1 L/S ratio was chosen for the ratio of leachate to solids in the anaerobic digestion reactor with a volume of 10 m^3. The ammonia concentration was assumed to be 10000 mg-N/L in the food waste. The ammonia concentration was 1000 mg-N/L in the leachate after recirculation. The linear velocity of the BMED operation remained at 1.4 cm/s and the membrane open area was selected as 275 cm^2. It was assumed that the BMED-SSAD was operated under steady-state conditions and that ammonia was only removed by the BMED stack. The example pilot-scale operating conditions are presented in Table 3.4.

After 20 days of the pilot-scale BMED-SSAD operation, the final ammonia concentration in the anaerobic digestion reactor would decrease proportionally as the number of cell pairs and current density increased (Figure 3.6). As the current density increased, the concentration of ammonia separated from the leachate would increase linearly (Figure 3.6A). At a given current density, the pilot-scale BMED resulted in a larger concentration of ammonia separated compared to the lab-scale BMED due to the difference in the membrane open area. Increasing the membrane open area by a factor of 7 (36 cm^2 in lab-scale compared to 275 cm^2 in pilot-scale) resulted in an increase in the volumetric flow rate by a factor of 2.5 and an increase of ammonia separation in the BMED stack by a factor of 3 (e.g. at 8 mA/cm^2 operation, 22 mg-N/L compared to 67 mg-N/L of ammonia separated).

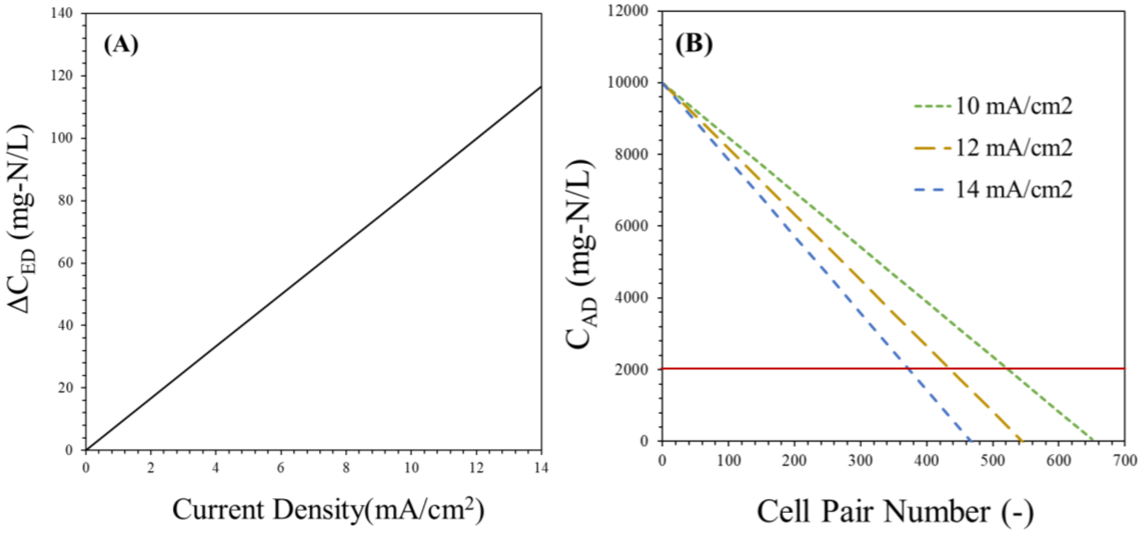

Figure 3.6 Pilot-scale BMED-SSAD: (A) The change in the leachate ammonia concentration (mg-N/L) relative to the current density in BMED with 36 cm^2 membrane open area. (B) The final Ammonia concentration in the anaerobic digestion reactor after HRT of 20 days. The red line represents a final ammonia concentration of 2000 mg-N/L.

The final ammonia concentration in the SSAD reactor would decrease proportionally as the number of cell pairs in the BMED increased (Figure 3.6B). For pilot-scale operations, it is suggested to operate the BMED stack with 450 cell pairs and 275 cm^2 of membrane open area at 12 mA/cm^2 to achieve a final ammonia concentration of less than 2000 mg-N/L in the anaerobic digestion reactor.

3.4.5 *Example calculations for power consumption*

For the suggested operating parameters in the example calculations (Section 2.4.3 and 2.4.4), the BMED electric power consumptions are presented in Table 3.5.

Table 3.5 The BMED electric energy consumption for various operating conditions in lab-scale and pilot-scale BMED-SSAD design.

System	Current density (mA/cm^2)	Cell pair #	Applied voltage per cell pair (V)	Energy consumption (kWh/kg-N)
Lab-scale BMED-SSAD	4	5	2.0	14
	6	4	2.6	21
	8	3	3.2	26
Pilot-scale BMED-SSAD	10	500	3.7	27
	12	450	4.3	31
	14	400	4.9	36

The lab-scale BMED-SSAD example calculations resulted in an electric consumption of 14 to 26 kWh/kg-N of ammonia separated. This is comparable to the electric energy consumption in the 8 BMED experiments. The experimental electric energy consumption for the stack operation ranged from 7 to 12 kWh/kg-N over the first 30 minutes and 10-16 kWh/kg-N for the 60 minutes operation.

The pilot-scale BMED-SSAD example calculations resulted in an electric consumption of 27 to 36 kWh/kg-N of ammonia separated. An increase in the number of cell pairs resulted in a decrease in electric energy consumption. However, the added cost of the cell pairs needs to be considered as well. The energy consumption could be further decreased by operating at an increased linear velocity. At a given applied voltage, the current density increases with increasing linear velocity.[19] Therefore, the electric energy consumption and the number of required cell pairs would decrease substantially, making the pilot-scale BMED-SSAD operation a feasible technology.

3.5 Conclusions

Various operating conditions were analyzed to assess the feasibility of a lab-scale and pilot-scale BMED-SSAD recirculation system through experiments and a numerical model. Example calculations were performed to suggest operating conditions in order to achieve a final ammonia concentration of 2000 mg-N/L in the SSAD reactor to avoid inhibition. The example calculations resulted in a lab-scale BMED operation with 4 cell pairs and 36 cm^2 of membrane open area at 6 mA/cm^2 with an electric power consumption of 21 kWh/kg-N. For the pilot-scale operation, the calculations resulted in a BMED operation with 450 cell pairs and 275 cm^2 of membrane open area at 12 mA/cm^2 with an electric power consumption of 31 kWh/kg-N. For the purpose of improving the energy consumption, it was recommended to increase the BMED linear velocity. The pH of the feed solution was found to decrease slightly after the BMED experiments that proved to be ideal to apply to leachate recirculation for enhanced SSAD biogas production. Therefore, the lab-scale and pilot-scale BMED-SSAD recirculation system was found to be a feasible method for ammonia separation and recovery and enhanced SSAD operation.

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Chapter 4. Conclusions

This chapter summarizes the research, highlights the limitations, and outlines the direction for future research.

4.1 Thesis Conclusions

This thesis provided findings and suggestions regarding the operation of a bipolar membrane electrodialysis stack to separate ammonia from high strength wastewater. Different applied voltages were studied in a series of experiments to optimize BMED stack operation, increase ammonia separation efficiency, and enhance ammonia recovery. BMED operation at 5.0 V per cell pair resulted in rapid ammonia separation of 87% in 30 minutes with a low energy consumption of 7.7 kWh/kg-N and a relatively high purity in the recovery of the ammonia solution. Additionally, eliminating AEMs and implementing CIP procedures following each experiment were effective to maintain stable electric current generation and consistent ammonia separation, implying successful organic fouling control on CEMs.

In the numerical model of the hypothetical BMED-SSAD system with leachate recirculation, various operating conditions were analyzed to assess the feasibility of the system. The example calculations resulted in a lab-scale BMED operation with 4 cell pairs and 36 cm^2 of membrane open area at 6 mA/cm^2 with an electric power consumption of 21 kWh/kg-N. For the pilot-scale operation, the calculations resulted in a BMED operation with 450 cell pairs and 275 cm^2 of membrane open area at 12 mA/cm^2 with an electric power consumption of 31 kWh/kg-N. Therefore, BMED was found to be a highly effective technology for ammonia separation for both dewatering centrate and leachate in SSAD operation.

4.2 Future directions

The results of this paper presented insights into optimized BMED operation and a unique approach to BMED application in anaerobic digestion. However, more work remains on the path to pilot and commercial implementation of the technology in the wastewater treatment industry. Further research should focus on recovery efficiency and purity of ammonium solutions. Additionally, more studies are needed on scaling and fouling characterization and control in BMED stacks with larger ion-exchange membranes. In anaerobic digestion with leachate recirculation, a more extensive numerical model with increased linear velocity and decreased operation time can be highly beneficial for paving the path to lab-scale and pilot-scale experiments.