

**Exploring Bioelectrochemical Systems for Removal and Recovery of
Hexavalent Chromium or Nutrients**

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ABSTRACT

Bioelectrochemical systems (BES) is a platform technology that is able to realize versatile engineering functions and recover valuable resources in an energy-efficient manner. One of the potential applications of BES is to remove and recover nutrients simultaneously from nutrient-rich wastewater, such as digested manure from livestock. A four-chamber BES was developed and used in this study to explore the potential to remove and recover hexavalent Chromium from synthetic wastewater, and ammonia and phosphate from digested manure. The BES was able to achieve 99.6% removal of Chromium by membrane adsorption in 5 days but failed to recover in the concentration chamber. Nutrients were removed from the waste stream and recovered in the recirculated catholyte by the electrical field generated from the waste. The BES was demonstrated to achieve substantial COD removal, nutrients removal and recovery. On average, the removal efficiencies were about 50% for COD, 85% for $\text{NH}_4\text{-N}$ and 40% for $\text{PO}_4\text{-P}$, and the concentration of $\text{NH}_4\text{-N}$ recovered in the catholyte was 670 mg/L after 5 cycles under an applied voltage of 0.8 V. $\text{PO}_4\text{-P}$ was not recovered in solution, probably because it has precipitated under the alkaline condition together with Mg^{2+} and Ca^{2+} concentrated in the catholyte. It was also demonstrated that nutrients removal and recovery depended on the current generation and were mostly completed at high current.

To sum up, the BES was proven to be an effective and sustainable approach to remove and recover nutrients from digested manure.

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Chapter 1

Introduction

1.1 Demand for nutrients removal and recovery

Eutrophication in water bodies has been a critical environmental issue since mid-20th century all over the world. Consequences of eutrophication include algae blooming and excessive growth of aquatic weeds and phytoplankton, which can cause pollution to drinking water and fish industry, increase turbidity of water bodies, decrease lifespan of lakes and exert adverse impacts to ecosystems[1, 2]. Such impacts upset local economy. Recently it was reported that the economic loss due to eutrophication in freshwaters in United States was estimated to be \$2.2 billion per year[3], highlighting an urgent need of eutrophication control in water bodies.

It has been recognized that excessive nutrients, such as nitrogen and phosphorus, discharged into receiving water bodies are the major cause of eutrophication. Nutrients may come from different point sources or non-point sources, depending on the local settings near receiving water bodies. Point sources include discharge of domestic wastewater, anaerobic digested sludge, swine wastewater, municipal landfill leachates, and run-off and infiltration from animal feedlots[2]. Typical non-point sources include run-off from agriculture and pasture. Due to the large volume and increased nutrients loadings, domestic wastewater is one of the major big contributors to nutrients discharge. Run-off from agriculture also generate large amount of nutrients because of the extensive use of fertilizer. Another primary contributor is the wastewater produced from livestock and poultry, featured by high strength and low C/N ratio. To control eutrophication, one

of the key tactics is to control the emission of nutrients from point sources into water bodies by implementing a wastewater treatment facility since they are usually continuous and can be directed and centralized into process units for treatment[4]. While non-point sources are usually difficult to control, such strategy may not be applicable. Therefore, there is a huge demand for nutrients removal from point sources that contribute large amount of nutrients prior to discharge to receiving water bodies. Furthermore, recent years have witnessed increasingly stringent discharge limits for nutrients, leading to urgent demand of not only building more treatment facilities but also developing sustainable technologies for nutrients removal.

It has become increasingly clear that wastewater can be a resource rather than a waste because of the organic energy and nutrients it contains. A number of drivers have emerged that emphasize the need to promote the recovery of nutrients in wastewater. For example, recovering ammonia directly from wastewater not only reduces the energy and chemical input for biological nitrification and denitrification, but also provides fertilizers for agriculture use. The recovery of phosphorus from wastewater is more beneficial due to the decreasing supply and increasing demand of mineral phosphorus, which is essential to sustainable food security as a limited source of critical material for fertilizer[5]. The amount of nutrients available in different types of wastewater is substantial. Rittmann et al. has reported that 15% of the phosphorus was discharged into sewage and sewage-treatment sludge and 40% of the phosphorus flows into animal waste, most of which is recoverable[6]. Therefore, the recovery of nutrients from waste stream may hold great promise to alleviate the burden of global nutrients need and reduce the cost for nutrients

manufacture. One of the examples is the commercial application of phosphorous recovery through magnesium ammonium phosphate (struvite) crystallization in dewatering reject streams[7].

1.2 Introduction to bioelectrochemical systems (BES)

Bioelectrochemical systems are a sustainable technology that uses bacteria in the anode as catalysts to directly convert chemical energy stored in waste materials into electricity or hydrogen gas or other outcome[8]. The basic model of a bioelectrochemical system is microbial fuel cells (MFCs), whose major benefit is electricity generation. Different models of BES have been derived from the MFCs, characterized by various uses of harvested electrons and potential across the electrodes to accomplish versatile functions. A BES using harvested electrons as a reductive force to catalyze reduction-based reaction in the cathode chamber so as to produce hydrogen gas or other value added chemicals is termed microbial electrolysis cells (MECs). A BES with an extra middle chamber and a pair of anion exchange membrane (AEM) and cation exchange membrane (CEM) installed between the anode and the cathode so that sea water can be desalinated under the electric force is termed microbial desalination cells (MDCs). Therefore, BES not only provides a unique environment to understand the largely unexplored microbial electrochemistry, but also offers a flexible platform for various engineering functions[9, 10]. Hence, researchers showed great interests in understanding and developing BES and extensive studies have been conducted in recent years.

Despite various models of BES developed for different functions, the electron transfer mechanisms in the anode in different types of BES are similar. To illustrate, Figure 1.1 shows a simple dual-chamber MFC. Biofilm attached on the anode is able to oxidize organics fed into the anode chamber which serve as electron donors, generally waste materials such as municipal wastewater, and electrons are released and transferred to the conductive anode such as carbon brush and carbon cloth by electron mediators or shuttles, by membrane-bound proteins or nanowires produced by the bacteria[11, 12]. These electrons flow to the cathode electrode spontaneously through the external circuit containing a resistor when an electron acceptor is present and the overall thermodynamics is favorable. Aeration is generally applied to the cathode chamber to provide dissolved oxygen as electron acceptor due to its high oxidation potential and availability. A CEM is required to separate the anode and the cathode compartments. Cations are driven by the electromotive force to migrate across the CEM to complete the current circuit. In an ideal condition, water would be the only end product in the cathode compartment since it was assumed that only protons would migrate. However, protons are just part of cations in real conditions, thus the elevation of pH of the catholyte is always observed. Different types of BES such as MECs and MDCs have the same anode configuration and function as MFC described above. Notice that the anode compartment should be kept anaerobic.

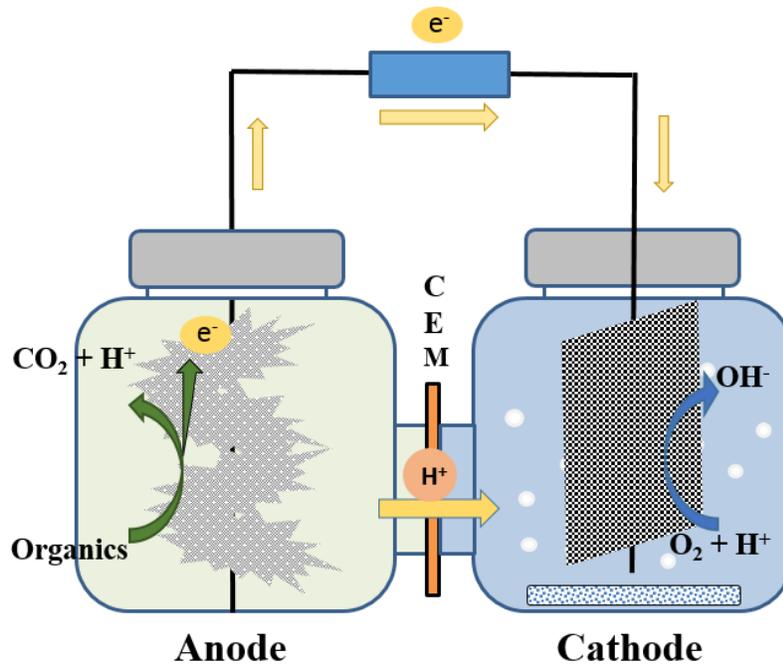


Figure 1.1 Schematic of dual-chamber microbial fuel cell

The most beneficial application of BES is wastewater treatment owing to its low energy input and less second sludge production compared to conventional activated sludge systems that are energy-intensive due to the massive need of aeration for oxidation and nitrification[13]. In addition, BES can reclaim resource values from wastewater to offset the energy cost to some extent. A BES is able to greatly reduce or in some cases eliminate the need for aeration, which accounts for roughly 50% of energy cost in a traditional wastewater treatment plant[14]. Besides, the anaerobic condition and biofilm-based anode allow low biomass production in a BES. It has been reported that the cell yield of electrochemically active bacteria (0.07–0.16 g VSS/g COD) is much less than that of activated sludge (0.35–0.45 g VSS/g COD), meaning that it can reduce sludge production by 50–70%[15]. In terms of the “bonus” provided by BES, Huggins et al.

reported that an MFC can produce 10–20% more energy that can be used for other processes[16]. BES could provide other benefits including nutrients removal and recovery, or hydrogen production for energy use, depending on the design.

BES has a potential to remove and recover nutrients from wastewater either based on ion migration driven by electricity generation, or diffusion driven by concentration difference across the membrane[17]. In this way, BES technology may be more competitive in terms of treatment efficiency since one of the practical challenges for BES application in wastewater treatment is the inefficient nitrification in the anaerobic anode. There are some other challenges for BES to be applied commercially. For example, at this stage the energy recovery in a BES is too low to make it practically competitive, and a benchmark power density of 1000 W/m³ can be realized only in bench-scale reactors instead of pilot-scale reactors[18-20]. Furthermore, the overall cost of a BES is still expensive for wastewater treatment mainly due to the high cost of cathode catalysts and membranes. Further researches are needed to address these problems.

1.3 Introduction to animal manure

Along with the population and economic growth, recent years have witnessed an increasing production of animal manure from expanding livestock and poultry. With abundant organic matters, various nutrients (Nitrogen, Phosphorous and Potassium), animal manure has high resource values that could be recovered as fertilizer for crop production and as energy sources such as biogas[21, 22]. However, serious environmental impacts may occur when the management of animal manure is not

optimized. For example, animal manure would be excessive for regionally due to high intensity of livestock population and excessive phosphorus compared to nitrogen in manure for crop intake[23, 24]. In this case, excessive manure applied to farmland will cause increased nutrients loadings to the receiving water bodies via runoff and leaching, leading to eutrophication. Therefore, excess manure needs to be either transported offsite or treated onsite. High transportation costs, seasonal application needs, odor concerns, and the potential liability of environmental impacts limit the feasibility of offsite transportation and discourage other farmers from using manure[25, 26]. On the other hand, the cost of onsite treatment needed to satisfy stringent discharge limits is relatively low, thus there is a growing interest in turning excess manure into valuable products.

Anaerobic digestion is widely applied as a pretreatment method of animal manure to stabilize organic matter in liquid manure, and reduce solid contents and pathogenic bacteria before manure can be spread in cropland as fertilizer. Another benefit is that the organic nitrogen and phosphorus in the manure are converted to inorganic forms that are readily available for crop uptake in the process. Hence, excess animal manure that needs onsite treatment generally comes from anaerobic digesters, abundant of ammonia and phosphate. A common approach to recover these inorganic ammonia and phosphate is struvite precipitation as proposed by several studies[27]. BES could be another potential technology to recover nutrients from digested manure, based on the wastewater characteristics that a large amount of nutrients are present in ionized forms and COD contents are high.

1.4 Research objectives

The overall goal of this study is to develop a BES that is able to achieve simultaneous nutrients removal and recovery from nutrients-rich digested manure. A four-chamber BES capable of concentrating both anions and cations was designed and fabricated. Compared with other BES design for nutrients removal and recovery reported in previous studies, the BES in the present study separated the anolyte with other streams, preventing ions from flowing into the anode which may result in adverse impacts to the bacteria.

The specific objectives include:

- 1) Investigate the performance and feasibility of the BES for ions removal and recovery by examining electricity production, ions removal and ions concentrations.
- 2) Explore the performance of nutrients removal and recovery under continuous mode so as to identify the maximum removal capacity and its feedback on BES performance.
- 3) Examine the influence of different operational conditions on nutrients removal and recovery in the BES and discuss optimization strategies of operational conditions and post treatment of the effluent.

The knowledge and results obtained from the study will allow further investigation of this technology in future research and applications.

1.5 Literature review

1.5.1 Principles of nutrients removal and recovery in BES

Although BES technology has been advancing rapidly due to extensive research all over the world, several challenges remain to hinder the practical applications of BES to wastewater treatment in commercial use. One of the major challenges is the lack of

capability of nutrients removal of anode biofilm. A BES is able to degrade organic matters in wastewater efficiently within a reasonable time frame, however, the anaerobic condition in the anode compartment impedes the bacteria from nitrification and enhanced biological phosphorus removal, which need oxygen input. However, recent studies have shown that it is feasible remove nitrogen and phosphorus in a BES. Kim et al. has reported that ammonia removal from wastewater is mainly through the ammonia loss across the separator driven by electric force or diffusion, or nitrification with oxygen supply intruding into the biofilm[28]. Meanwhile, nitrate can accept electrons from organic compounds and be reduced to nitrogen gas, thus it is possible to use nitrate as a terminal electron acceptor in a BES based on such electron-transferring process[29]. Bioelectrochemical denitrification was demonstrated possible when Gregory et al. and Park et al. discovered that nitrate was reduced to nitrite with an electrode as the only electron donor by a pure culture of *Geobacter metallireducens* and mixed culture respectively[30, 31]. Unlike conventional denitrification that relies on heterotrophic denitrifying bacteria, bioelectrochemical denitrification relies on autotrophic denitrifying bacteria that are capable of accepting electrons from an electrode. Therefore, a denitrifying biocathode in an MFC was developed and studied by researchers, and simultaneous effective nitrate reduction and electricity generation was demonstrated[32, 33].

Considering the relatively high energy input and nitrogen footprint in nitrogen removal through nitrification and denitrification, recovering nitrogen from wastewater is considered to be a more sustainable approach. The recovered nitrogen in a BES is in form

of ammonia, which may be applied as a fertilizer to agricultural production. As mentioned above, the foundation for removing and recovering ammonia from wastewater in a BES is the fact the ammonia ions can migrate across a CEM driven by current generation or diffusion. Cord-Ruwisch et al. demonstrated the feasibility of ammonia removal via this mechanism in an MFC. It was found that ammonia acted as a proton shuttle accounted for about 90% of ionic flux in this system[34]. Cheng et al. developed such system by adding a gas-exchange device to recycle ammonia gas back to the anode for pH control, and showed the possibility of ammonia recovery[35]. Notice the ammonia migration from the anode to the cathode was against the concentration gradient and thus the success of ammonia recovery relied strongly on current generation. The same concept was also demonstrated feasible in an MEC. Villano et al. reported an ammonia accumulation of 318 mg/L in the cathode compartment, which was approximately ten times the ammonia concentration in the anode[36].

The study on phosphorus removal and recovery by a BES is relatively limited, but there is a certain interest and there are researchers working on that. Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) precipitation is a common approach for phosphorus recovery attracting increasing interest in recent years. Struvite precipitation has also been widely adopted in the investigation of phosphorus recovery in BES, as BES has the potential to generate high pH condition and provide raw materials for the process. Cusick et al. accomplished struvite formation in a BES with a single-chamber MEC, in which up to 40% of soluble phosphate was removed with a struvite precipitation at a rate of $0.3\text{--}0.9 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ [37]. Compared to a MFC, a MEC is able to maintain high pH condition due to the production of hydrogen from water

in the cathode compartment, indicating a MEC-based BES may be more suitable for struvite formation. It has been demonstrated that the role of a BES in struvite precipitation is to maintain a high-pH zone necessary for struvite formation. Another approach for phosphorus recovery in BES is based on the exchange of hydroxide ions produced from the cathode reaction with phosphate ions from wastewater proposed by Zhang et al.[38], which could remove $52.4 \pm 9.8\%$ of the phosphate.

1.5.2 BES applications to nutrients removal and recovery

Based the feasibility studies of nutrients removal and recovery in BES, researchers has applied BES to treatment of different types of real wastewater that is rich in nutrients as a method to recover ammonia and phosphorus simultaneously. These studies have successfully achieved reconcentration of nutrients in a single chamber that could be reused through further treatment, as reviewed in the following paragraphs.

Chen et al. developed a microbial nutrient recovery cell utilizing ion migration across membranes driven by current generation and ion exchange that can simultaneously treat wastewater and recover ammonia and phosphate taking advantage of the energy contained in wastewater. The removal efficiencies was $>82\%$ for COD, $>96\%$ for NH_4^+ -N, and $>64\%$ for PO_4^{3-} -P[39]. The concentrations of NH_4^+ and PO_4^{3-} in the recovery chamber increased by more than 1.5 and 2.2 times, respectively, compared to the initial concentrations in wastewater.

Tice et al. achieved energy efficient nutrient reconcentration from human urine using ion exchange membranes in a MEC where substrate oxidation at the MEC anode provides energy for the separation of nutrient ions[40]. The rate of nutrient separation was enhanced by increasing the number of the ion exchange membrane pairs and external voltage. Ammonia and phosphate were reconcentrated from diluted human urine by a factor of up to 4.5 and 3.0, respectively, when the applied voltage was 1.2V and 3 pairs of ion exchange membranes were used. The energy requirement normalized by the mass of nutrient reconcentrated was 6.48 MJ/kg-N (1.80 kWh/kg-N) and 117.6 MJ/kg-P (32.7 kWh/kg-P).

Zhang et al. developed a new type of BES (“R²-BES”) that took advantage of current generation to drive ammonium migration out of wastewater, and used hydroxide ions produced from the cathode reaction as a medium to exchange phosphate ions from wastewater[38]. Under an applied voltage of 0.8 V, the R²-BES removed $83.4 \pm 1.3\%$ of ammonium nitrogen and $52.4 \pm 9.8\%$ of phosphate, significantly higher than those ($3.6 \pm 3.7\%$ and $21.1 \pm 2.6\%$, respectively) under an open circuit condition. Applying an external voltage can increase current generation, COD removal, and nutrient removal.

Chapter 2

Feasibility study and performance study of the BES

2.1 BES treating Hexavalent Chromium

2.1.1 Introduction

Hexavalent Chromium-containing materials are widely used in a variety of industries such as electroplating, steel and other metal alloy production, leather tanning, cement, dye/pigment manufacturing, mining, photographic materials, paints, and fungicide production[41, 42]. Discharge of wastewater containing Cr(VI) would pose a serious threat to public health and ecosystems since the pollutant is non-biodegradable, highly toxic, of carcinogenic effect and being and highly corrosive in water[41]. Due to these adverse effects, EPA identified Cr(VI) as one of the seventeen chemicals posing the greatest threat to human health. The regulatory maximum Cr(VI) concentration in treated and ambient water is below 50 µg/L[43].

The removal of Cr(VI) from wastewater is challenging. Conventional technologies for industrial wastewater treatment are typically physicochemical processes including chemical precipitation, ion exchange, electrochemical separation and so forth. The most commonly used technology is chemical precipitation during which Cr(VI) is reduced to Cr(III) thus becomes less hazardous. However, due to relatively low concentration of Cr(VI) in wastewater and stringent regulations, these conventional technologies may be economically or environmentally disadvantageous due to the high energy input and the generation of secondary pollutants[44]. Therefore, there is a growing interest in developing sustainable technologies for Cr(VI) treatment. BES as a platform technology

featured with its sustainability and flexibility has a potential to achieve sustainable Cr(VI) treatment. BES with a biocathode that can accomplish reductive removal of contaminants is applied to Cr(VI) treatment. Huang et al. observed achieve nearly complete removal of Cr(VI) at a reduction rate of 19.7 mg/L·d[45]. Another possible approach would be using ion migration in a MDC-based BES to achieve Cr(VI) removal.

As a matter of fact, the original goal of the present study was to remove Cr(VI) using the four-chamber BES since the reactor configuration allowed anions in the desalination chamber to migrate across the AEM to the concentration chamber, but would be stopped by a CEM from migrating to the anode. The benefit of the design is that the toxic anions will not meet the functional biofilm and they could be concentrated for further treatment. Such an approach has a potential to reduce the treatment cost.

2.1.2 Materials and method

2.1.2.1 BES Setup

Lu et al. reported a plate-type four-chamber MDC capable of achieving simultaneous organic removal and desalination in the same synthetic wastewater. In this MDC, the anolyte is recirculated through the anode and the desalination chambers, while the catholyte is circulated between the cathode and the concentrating chambers[46]. Inspired by this design, a similar BES was fabricated, but operated in a different way in order to achieve simultaneous nutrients removal and recovery. The BES consisted of an anode chamber, a concentration chamber, a desalination chamber and a cathode chamber, as shown in Fig. 2.1. All the chambers were made of high-density polyethylen (HDPE), and

had the same dimension of $8.5 \times 4.5 \times 0.8$ cm. The anode and the cathode chambers were adjacent to cation exchange membranes (CEM, Membrane International Inc., Glen Rock, NJ, USA). The concentrating chamber and desalination chamber were separated by an anion exchange membrane (AEM, Membrane International Inc.). All the ion exchange membranes had the same sectional area of 38.25 cm^2 . A carbon brush (Gordon Brush Mfg. Co., Inc., CA, USA) and a 32-cm^2 carbon cloth (Zoltek Companies, Inc., MO, USA) with $5 \text{ mg}\cdot\text{cm}^{-2}$ of Pt/C (10% wt. Pt on Carbon Vulcan, Fuel Cell Earth LLC, USA) were used as the anode electrode and cathode electrode, respectively. The anode electrode was connected to a $1\text{-}\Omega$ resistor and then to the cathode electrode. Such a small external resistor was used to maximize current generation, which is the driving force for desalination.

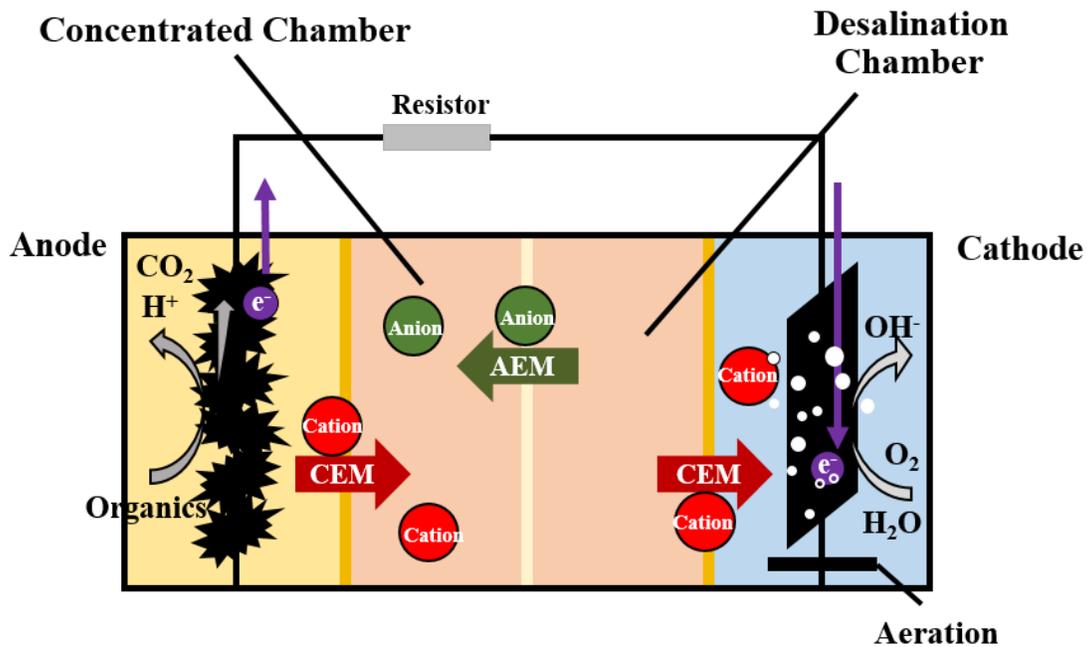


Fig. 2.1 Configuration and schematic of the four-Chamber BES

2.1.2.2 BES Operation

A synthetic domestic wastewater was used as the anolyte: 0.33 g L⁻¹ glucose, 0.09 g L⁻¹ NH₄Cl, 0.30 g L⁻¹ NaCl, 0.5 g L⁻¹ MgSO₄, 0.015 g L⁻¹ CaCl₂, 0.02 g L⁻¹ KH₂PO₄, 0.03 g L⁻¹ K₂HPO₄, 0.06 g L⁻¹ NaHCO₃ and 1 mL L⁻¹ trace element[47]. The synthetic wastewater has a COD concentration of 350 mg L⁻¹, a conductivity of 1.40-1.45 mS cm⁻¹ and a pH of 7.5-8.0. A hexavalent Chromium solution with 20mg·L⁻¹ Cr(VI) was prepared to mimic wastewater from industrial process such as electroplating and was used as the feed for the desalination chamber. A Cr(VI) stock solution of 200 mg·L⁻¹ was prepared by dissolving 0.318 g of analytical grade Na₂CrO₄ in 500 mL distilled water. The hexavalent Chromium solutions for feed were prepared by diluting the stock solution. The BES was inoculated with the digested sludge from a local wastewater treatment plant (Peppers Ferry, Radford, VA, USA).

After startup stage, the system reached steady performance and 45 mL of 20 mg·L⁻¹ hexavalent Chromium solution was fed into the desalination chamber, before which 1 g·L⁻¹ NaCl solution was fed into the desalination chamber to better monitor the performance. 45 mL of 1g/L NaCl solution was fed into the concentration chamber as the initial solution to provide necessary conductivity so that it would not hinder the performance of the system. The use of 1 g·L⁻¹ NaCl solution was to mimic secondary effluent from a municipal wastewater treatment plant. The catholyte (180 mL) containing 50 mM phosphate buffered saline (PBS, 2.65 g·L⁻¹ KH₂PO₄ and 5.35 g·L⁻¹ K₂HPO₄) recirculated between the cathode chamber and an external reservoir with constant aeration. The anolyte had a volume of 130 ml and also recirculated between the anode

chamber and an external reservoir. The recirculation rate of the anolyte and the catholyte was 20 mL·min⁻¹. No recirculation was introduced to desalination chamber and concentration chamber. The anolyte was replaced every 24 hours.

The BES was run in an MFC mode, 1-Ω resistor was connected to the external circuit as a small load to maximize the desalination efficiency. No extra voltage was applied to the system.

2.1.2.3 Measurements and analysis

The voltage across the external resistor (1Ω) was recorded every 5 min by a digital multimeter (2700, Keithley Instruments Inc., Cleveland, OH, USA). The current (I) of the BES was calculated with $I = U/R$. The concentration of the Hexavalent Chromium was measured using a DR/890 colorimeter (HACH Co., Ltd., USA) according to the manufacturer's instruction. The pH and conductivity were measured by a bench top pH meter (Oakton Instruments, Vernon Hills, IL, USA) and a bench-top conductivity meter (Mettler-Toledo, Columbus, OH, USA), respectively.

2.1.3 Results and discussion

According to the process shown in Fig. 2.1, it was expected that CrO₄²⁻ would be removed from the desalination chamber and concentrated in the concentration chamber via ion migration under the electric force. When operated in consecutive cycles, the concentrating solution was sustained in the concentration chamber while the solution in the desalination chamber was replaced at the end of every cycle. It was expected that the

concentration chamber would reconcentrate considerable amount of Cr(VI) after a few cycles, so that further treatment of Cr(VI) would be easier owing to higher concentration compared to raw wastewater. According to Fig. 2.2, the BES was able to achieve nearly complete Cr(VI) removal in the desalination chamber in five days with a removal efficiency of $99.6\% \pm 0.02\%$, leading to a effluent Cr (VI) concentration slightly above the regulatory maximum Cr(VI) concentration in treated and ambient water of 50 ug/L. The figure showed a slower removal speed when then concentration of Cr(VI) become low and it took a long time to be removed to the regulatory level, possibly because the conductivity of the Cr(VI) solution decreased, and the current generation of the system as well as the efficiency of ion migration were hindered. According to Fig. 2.5, the peak current was below 0.6 mA, indicating a poor current generation of the system. This is because the conductivity of the Cr(VI) solution was very low (98.2 ± 8.4 us/cm in the beginning) since Na_2CrO_4 was the only solute in the dionized water. Although Cr(VI) removal was achieved from the desalination chamber, the BES failed to recover Cr(VI) in the concentration chamber. As shown in Fig. 2.3, no Cr(VI) was detected in the concentration chamber during the whole cycles, implying that CrO_4^{2-} might not migrate across the AEM to the concentration chamber. A possible reason might be that CrO_4^{2-} was adsorbed by the membrane. It was reported that in an electro dialysis process where an AEM was used to recover chromic acid, the AEM showed a poor stability against the oxidative chromic acid solution and the increase of the AEM resistance, especially at the starting phase of the process, due to the formation of polychromates in the membrane[48, 49]. A previous work also showed that an AEM in contact with CrO_3 solutions was progressively filled by polychromate ions $\text{Cr}_n\text{O}_{3n+1}$. The presence of these polychromate

ions may make the AEM become amphoteric, as the second negative charge of the polychromate ions can act as a mobile exchange site[50]. These findings implied that during the CrO_4^{2-} migration, CrO_4^{2-} would first form polychromate ions inside the AEM and then serve as the bridge to transfer remaining CrO_4^{2-} in the bulk solution across the membrane after the membrane was filled with polychromate ions. A previous study showed that the formation of polychromate ions was favored by membrane absorption, leading to a high concentration within the membrane[51].

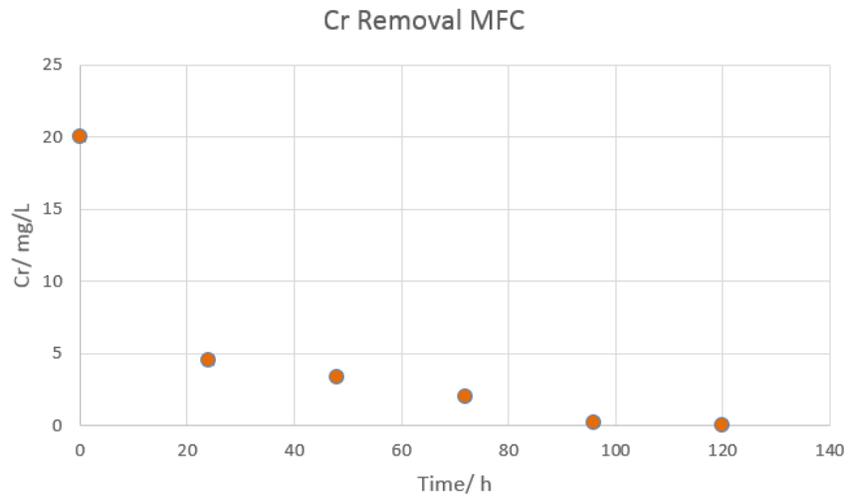


Fig. 2.2 Cr(VI) removal in desalination chamber in 5 days

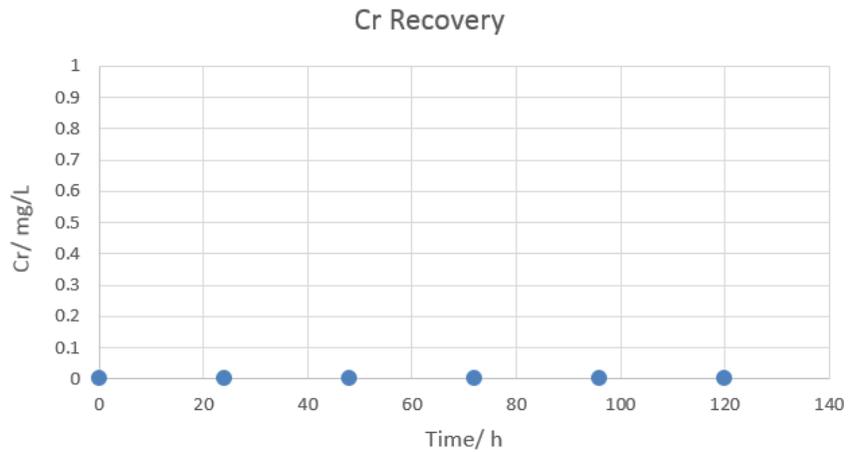


Fig. 2.3 Cr(VI) recovery in concentration chamber in 5 days

To verify the possibility of membrane absorption, a comparison of Cr(VI) removal in the desalination chamber under the MFC mode and open circuit condition was conducted. Notice that no current was generated under the open circuit condition. Results showed that even in the absence of electric current, Cr(VI) removal could also be achieved in the desalination chamber (Fig. 2.6). However, compared to the removal rate under MFC mode (Fig. 2.4), the removal rate under open circuit condition was lower, indicating that the electric current increased the Cr(VI) removal in desalination chamber. Notice that in Fig. 2.5, the current showed a sudden rise every time after sampling, because the sampling procedure using a syringe introduced mixing into the chamber. After dismantling the reactor, it was found that the membranes, including the AEM and the CEM, turned yellow, which was the color of chromate ions. These findings demonstrated that Cr(VI) in the desalination chamber was likely removed by the absorption of both the AEM and the CEM, probably in the form of polychromate ions. The electric current had a positive impact on Cr(VI) removal by accelerating the movement of chromate ions onto the AEM. Considering the low concentration of Cr(VI) and low volume of the chamber, it would take a long time to reach the absorption capacity of the membrane. Hence, it was demonstrated that the BES was not feasible to recover Cr(VI) in wastewater.

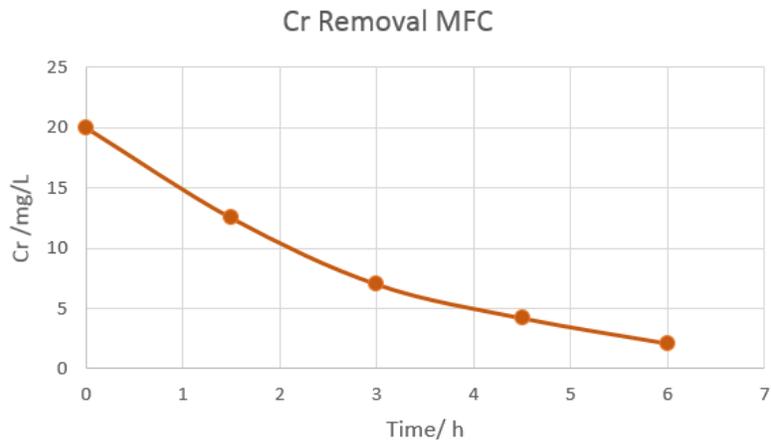


Fig. 2.4 Cr(VI) removal in desalination chamber under MFC mode in 6 hours

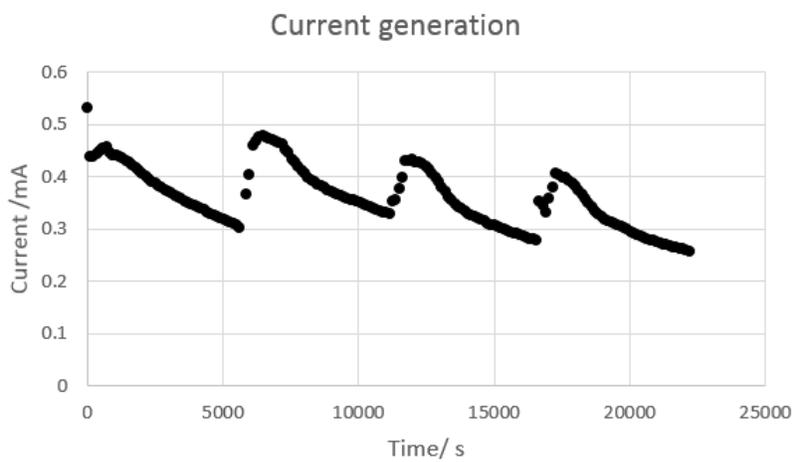


Fig. 2.5 Current generation under MFC mode in 6 hours

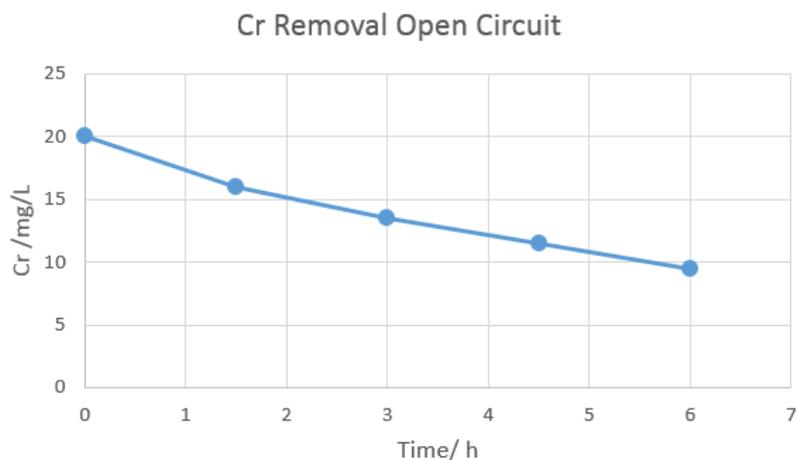


Fig. 2.6 Cr(VI) removal in desalination chamber under open circuit in 6 hours

2.2 BES treating digested manure

2.2.1 Materials and Methods

2.2.1.1 BES Operation

Because the AEM was contaminated by Cr(VI), all the ion exchange membranes were replaced with new ones and the BES was reassembled. The BES was re-inoculated with digested manure collected from the effluent of an anaerobic digester run from a research group of the Department of Biological Systems Engineering, Virginia Tech, and digested sludge from a local wastewater treatment plant (Peppers Ferry, Radford, VA, USA). During the startup stage, the digested sludge was removed and only the digested manure was fed into the anode. An external voltage of 0.8V was applied to the system to accelerate the acclimation. The positive pole of the power supply was connected to the anode of the BES while the negative pole was connected to the resistor adjacent to the cathode.

The performance of the BES was evaluated after the system reached a steady stage. At first, the BES was run under an MFC mode with an applied voltage of 0.8V. The anode chamber was fed with 150 ml of liquid fraction of digested manure. Only 100 mL stored in the external reservoir was replaced at the end of every cycle and was amended with additional $4.2 \text{ g}\cdot\text{L}^{-1}$ NaHCO_3 as the buffer. The hydraulic retention time was 48 hours. Digested manure was centrifuged for 30 min at 8000 rpm to separate the solid fraction and the liquid fraction. NaCl solutions ($10 \text{ g}\cdot\text{L}^{-1}$) were pumped into the cathode chamber, the desalination chamber and the concentration chamber as the initial solution, all of which were connected with an external reservoir and recirculated at a flow rate of $20 \text{ mL}\cdot\text{min}^{-1}$. The volumes of the desalination chamber, the concentration chamber and the cathode chamber were 150 mL, 150 mL and 180 mL, respectively.

Then the BES was run under an MEC mode with an applied voltage of 0.8 V in order to evaluate the performance of reconcentration of ions removed from desalination chamber and anode chamber. The operation of the anode and the desalination chamber was the same as described under the MFC mode. However, the concentration chamber and the cathode chamber did not have external reservoirs and were hydraulically connected and recirculated at a flow rate of $20 \text{ mL}\cdot\text{min}^{-1}$. A lower concentration of NaCl solutions ($5 \text{ g}\cdot\text{L}^{-1}$) was sparged by nitrogen gas to expel the dissolved oxygen before fed into both chambers and all of them were replaced at the end of every cycle. Enclosed and no aeration introduced, an anaerobic environment was formed inside both chambers, allowing the reaction of hydrogen production. A gas bag was connected to the cathode chamber to collect the hydrogen produced during the MEC process. The volume of the

desalination chamber was 150 mL and the total volume of the concentration chamber and the cathode chamber was 112 mL.

In the third stage of the study, the BES was run under an MEC mode to evaluate the performance of nutrients removal and recovery from digested manure (Fig. 2). It was expected that NH_4^+ would migrate from the anode chamber to the concentration chamber and from the desalination chamber to the cathode chamber across the CEMs. It was also expected that the phosphate would migrate from desalination chamber to the concentration chamber across the AEM. Recirculation of the catholyte between the cathode chamber and the concentration chamber combined two separate streams into one single stream, introducing hydroxide ions for ion exchange with phosphate and enhancing the capacity of nutrients recovery. The anode chamber was fed with 110 mL of liquid fraction of the digested manure. Only 60 mL stored in the external reservoir was replaced with new feed at the end of every cycle and amended with extra $2.8 \text{ g}\cdot\text{L}^{-1}$ NaHCO_3 as the buffer. The hydraulic retention time was 48 hours. The desalination chamber was fed with the effluent from the anode chamber. Only 45 mL of the feed for the desalination chamber stored in the external reservoir was refreshed every cycle. The other operation settings were the same as described in the previous stage under the MEC mode.

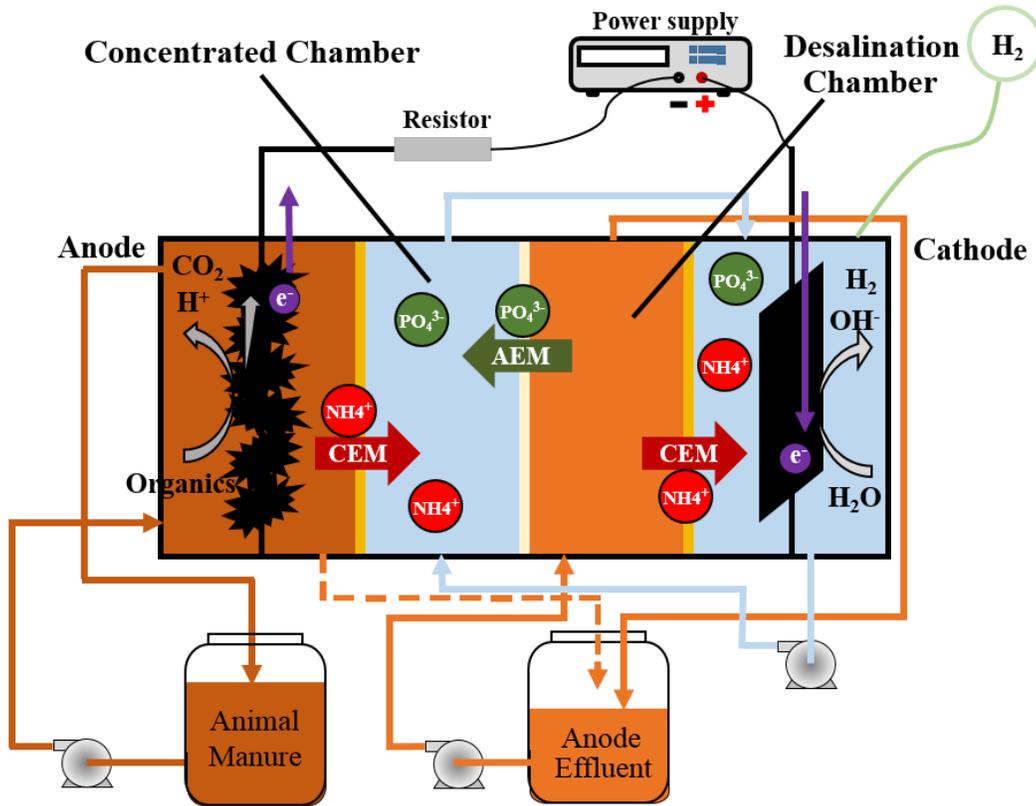


Fig. 2.7 Configuration and schematics of BES in MEC mode treating digested manure

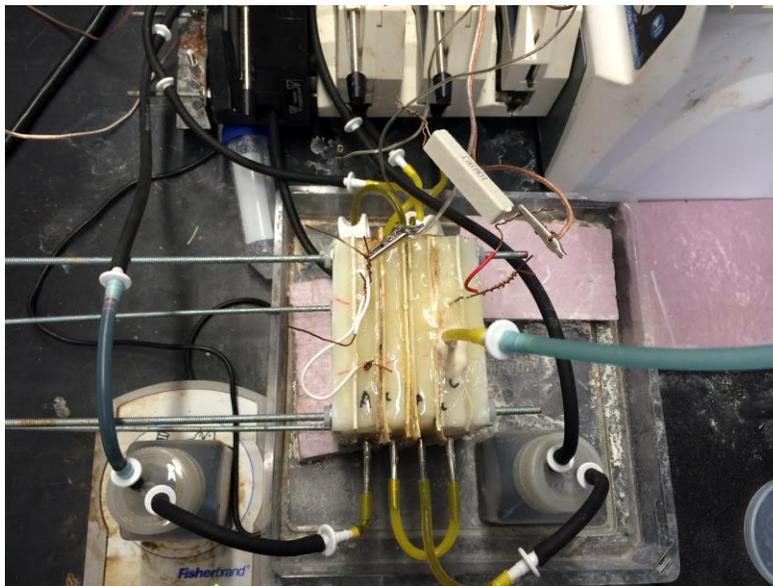


Fig. 2.8 Top view of BES in MEC mode treating digested manure

2.2.1.2 Measurements and analysis

The voltage across the external resistor (1 Ω) was recorded every 5 min by a digital multimeter (2700, Keithley Instruments Inc., Cleveland, OH, USA). The current (I) of the BES was calculated with $I = U/R$. The concentrations of chemical oxygen demand (COD), ammonia nitrogen and phosphate were measured using a colorimeter according to the instructions of the manufacturer (Hach Company, Loveland, CO, USA). Measurements of phosphate followed the Low Range Total Phosphate Method in the instructions. The pH and conductivity were measured by a bench top pH meter (Oakton Instruments, Vernon Hills, IL, USA) and a bench-top conductivity meter (Mettler-Toledo, Columbus, OH, USA), respectively.

Coulombic efficiency (CE) was calculated according to a previous work[8]. The CE is defined as the ratio of the total Coulombs transferred from the anode to the cathode, to the maximum possible Coulombs of the substrate oxidation. The total transferred Coulombs was determined by integrating the current over time, so that the Coulombic efficiency for an MFC run in fed-batch mode, evaluated over a period of time t_b , is calculated as

$$CE = \frac{M \int_0^{t_b} I dt}{F b V \Delta COD} \quad (3.1)$$

where M (32) is the molecular weight of oxygen, I is the electric current, F is the Faraday's constant, b (4) is the number of electrons transferred per mole of oxygen reduction, V is the volume of liquid in the anode compartment, and ΔCOD is the change in COD over time t_b .

2.2.2 Results and Discussion

2.2.2.1 Current generation of the BES

Current generation was first examined to evaluate the performance of the BES, because the current produced from the digested manure was the driving force of ions migration, thus it was expected to be a key factor of nutrients removal and recovery. In theory, higher current would result in the higher efficiency of nutrients removal and recovery. With a high ratio of the membrane area to volume of chambers and high influent COD, the BES was expected to achieve high current generation[52]. The BES was run under an MFC mode with an applied voltage of 0.8 V and an MEC mode with the same applied voltage. The results showed that the BES achieved high current generation both under the MFC mode (Fig. 2.8) and MEC mode (Fig. 2.9). The peak current achieved under MFC mode was 15 mA with a CE of $14.71\% \pm 0.12\%$. The removal of conductivity in a 48-hour cycle was $99.81\% \pm 0.04\%$, attributed to a strong driving force of ion migration (high current). Although the current generation was high, the CE was relatively low, indicating that non-exoelectrogenic bacteria grew or alternate electron acceptors other than the electrode were present[53]. Under the MEC mode, the peak current achieved was about 8 mA and the CE was $14.92\% \pm 0.08\%$, showing a lower current generation but a similar coulombic efficiency compared to the MFC mode. The reason for a lower current generation might be the lower reduction potential of H^+/H_2 under the MEC mode, compared to that of O_2/OH^- under the MFC mode. Meanwhile, the salinity removal achieved under the MEC mode was $88.81\% \pm 0.86\%$, indicating that the driving force generated under the MEC mode was sufficient for desalination and nutrients removal.

These findings demonstrated that the BES may hold potential in nutrients removal and the treatment of digested manure.

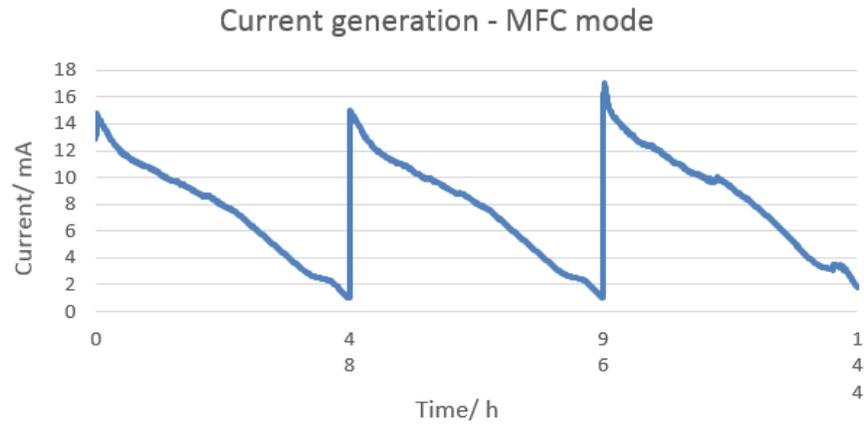


Fig. 2.9 Current generation under MFC mode

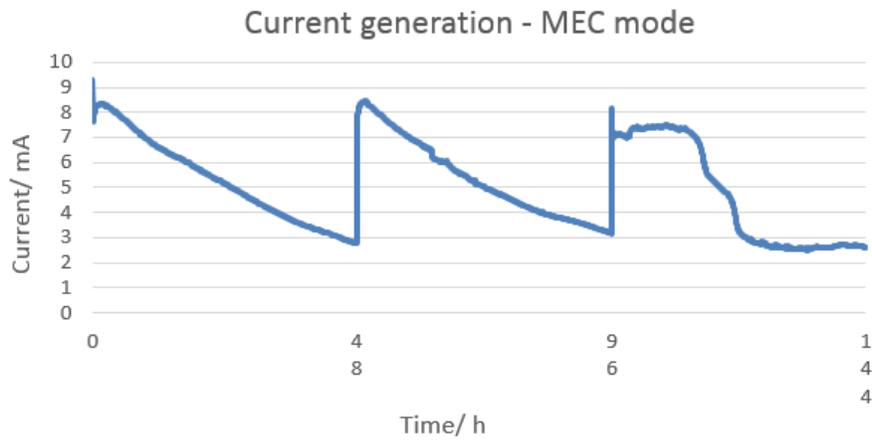


Fig. 2.10 Current generation under MEC mode

2.2.2.2 Nutrients removal and recovery in a single cycle

To test the feasibility of nutrients removal and recovery using the BES, the performance of nutrients removal and recovery in a single cycle was evaluated. Notice in this phase, the organic loading was reduced (only 60 mL of the anolyte was replaced with new digested manure) due to the limited source. The results showed that the current generation was lower than previous cycles (Fig. 2.9): the peak current was 4.5 mA and the current generation seemed to decrease in the subsequent cycle. Possible reasons included the reduced organic loading which diminished substrate concentration, and reduced conductivity of the solution in cathode chamber/concentration chamber and desalination chamber. It was not clear why the current generation decreased over cycles. Interestingly, after turning the BES to the open circuit conditions for 48 hours to reach the OCV (open circuit voltage, usually 0.8V in a BES), the current generation of the BES was recovered. The reason warrant further studies.

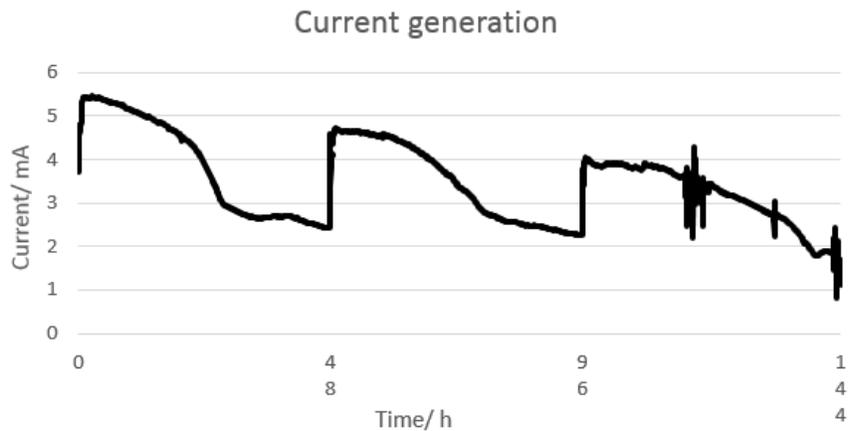


Fig. 2.11 Current generation in nutrients removal and recovery phase

The BES was able to achieve a COD removal of $49.59\% \pm 3.10\%$ in the anode (Fig. 2.12) in a 48-hour cycle, with an effluent COD of 4840 ± 180 mg/L. Considering the high COD in the digested manure, COD removal was considerably high, indicating active bacterial metabolism in the biofilm. Compared to the high COD removal in the anode, the desalination chamber did not significantly remove the COD. The COD removal in the desalination chamber might result from the metabolism of the remaining bacteria and the migration of ionized volatile acids to the adjacent chambers. The results also showed changes of pH in the catholyte and desalination chamber. According to Fig. 2.13, the pH was elevated to 10.04 ± 0.02 in the catholyte, and to 9.49 ± 0.02 in the desalination chamber. The pH change in the desalination chamber was due to the ion exchange across the AEM, which was likely to be the mechanism of phosphate removal[13].

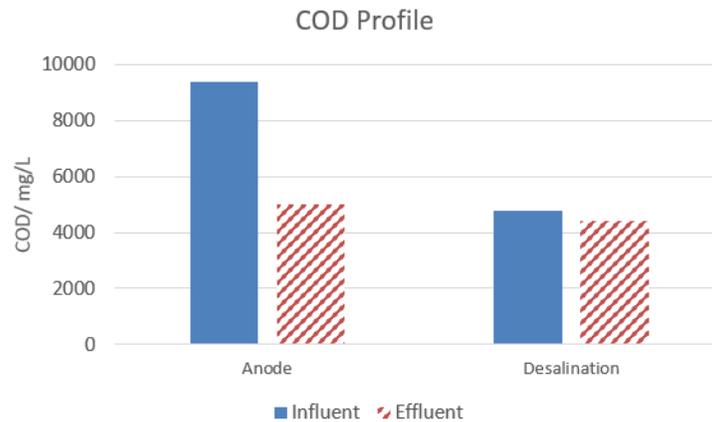


Fig. 2.12 COD profile in a single cycle

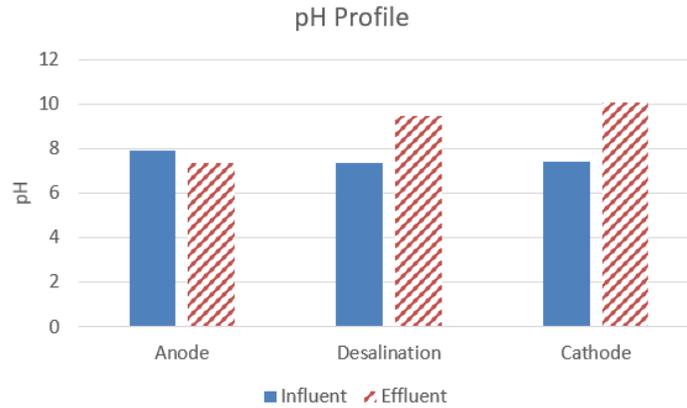


Fig. 2.13 pH profile in a single cycle

The results also demonstrated that the BES was able to achieve considerable nutrients removal and recovery. As shown in Fig. 2.14, high ammonia removal was achieved and ammonia recovery was observed in the catholyte. In a 48-hour cycle, the anode was able to remove 66.67% of the $\text{NH}_4\text{-N}$, while the desalination chamber was able to remove $75.95\% \pm 2.62\%$ of the $\text{NH}_4\text{-N}$ from its influent. When normalized, the desalination chamber removed 19.64% of ammonia of raw digested manure. Namely, the ammonia removal by the anode was 3.4 times higher than that by the desalination chamber. In total, the BES was able to achieve $86.31\% \pm 1.22\%$ $\text{NH}_4\text{-N}$ removal from the raw digested manure after 2 operation cycle, or a complete cycle of digested manure staying in the BES. The final effluent contained $80 \pm 20 \text{ mg}\cdot\text{L}^{-1}$ of $\text{NH}_4\text{-N}$, which was a low level compared to its concentration in the influent ($840 \pm 20 \text{ mg}\cdot\text{L}^{-1}$). The concentration of $\text{NH}_4\text{-N}$ in the recovery solution was up to $230 \pm 10 \text{ mg}\cdot\text{L}^{-1}$, leading to a recovery percentage of $59.22\% \pm 2.57\%$. This may imply that about 60% of ammonia removed from the wastewater was via the path of migrating across the membrane under the electromotive force. The percentage of recovery obtained here was higher than that

reported in similar studies[13, 39, 40], probably due to the high concentration of ammonia present in digested manure. Other possible paths of ammonia removal included the intake by microorganisms, physical adsorption, chemical precipitation, membrane fouling, etc. Compared to ammonia removal, salinity (present as conductivity) removal was lower in the anode and the desalination chamber, indicating ammonia was a relatively easy specie to be driven across the membrane by electric field. These results proved that the BES had a strong capacity of ammonia removal and recovery. Phosphate removal and recovery was not shown and discussed in this section, because the measurements using Hach Low Range Total Phosphate Method did not yield reliable results. In the following trials, Hach High Range Total Phosphate Method would be adopted for phosphate measurements.

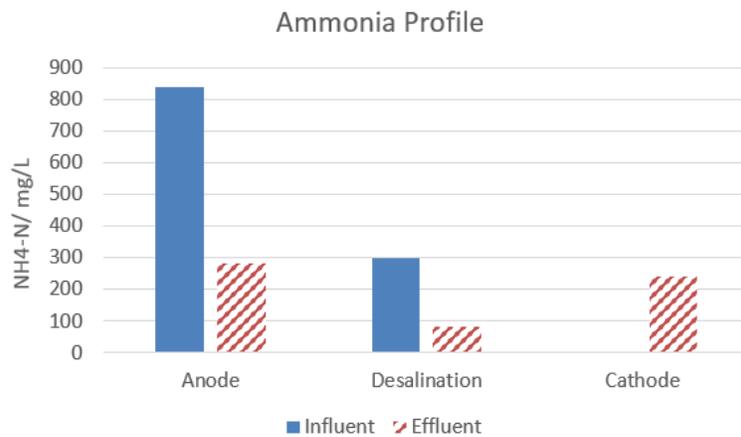


Fig. 2.14 $\text{NH}_4\text{-N}$ profile in a single cycle

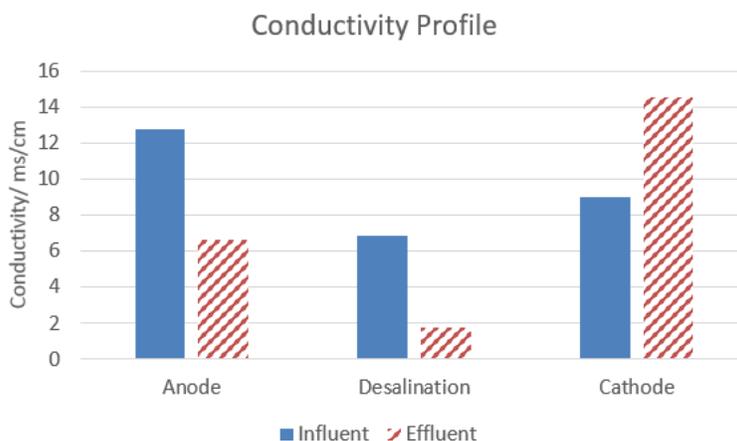


Fig. 2.15 Conductivity profile in a single cycle

2.3 Conclusions

The BES was able to achieve nearly complete Cr(VI) removal in the desalination chamber, however, failed to recover Cr(VI) in the adjacent concentration chamber. Comparison of the BES performance under the MFC mode and the open circuit conditions showed that Cr(VI) was possibly removed by membrane absorption while current generation was accelerating the process, since it was reported that chromate ions would first form polychromate ions in the AEM and serve as a bridge to transport chromate ions after the AEM was filled.

The BES was proven feasible to achieve nutrients removal and recovery from digested manure. The BES was able to achieve high current generation, which was the driving force of ion migration, and high salinity removal treating digested manure. Nutrients removal and recovery tests in a single cycle demonstrated that the BES was able to

achieve 50% COD removal, and 86% NH₄-N removal in total, 60% of which was recovered in the catholyte. The elevation of pH in the cathode chamber and the desalination chamber revealed the ion exchange process across the AEM, indicating the potential of phosphate removal via ion exchange.

Chapter 3

Nutrients removal and recovery from digested manure using the BES

3.1 Materials and Methods

3.1.1 BES Operation

The BES was run under MEC mode as described in 2.2.1.1. The difference was that the catholyte recirculated between the cathode chamber and the concentration chamber was not replaced at the end of every cycle. Instead, the catholyte were kept in the system for 5 consecutive cycles to recover as much nutrients as possible. Moreover, $1\text{g}\cdot\text{L}^{-1}$ NaCl solution pre-sparged by nitrogen gas for 15 minutes was used as the initial catholyte instead of $5\text{g}\cdot\text{L}^{-1}$ NaCl solution, because it was not economical to use $5\text{g}\cdot\text{L}^{-1}$ NaCl solution in practice but reasonable to use $1\text{g}\cdot\text{L}^{-1}$ NaCl solution, whose conductivity was similar to the secondary effluent from a municipal wastewater treatment plant, which was of practical significance. At the end of every cycle, 5 mL of the catholyte was sampled using a 10-mL syringe for measurement and 5 mL of $1\text{g}\cdot\text{L}^{-1}$ NaCl solution was reinjected into the concentration chamber for replenishment. The pH of samples was adjusted to neutral before testing. In this way, the performance of nutrients removal and recovery in different chambers and in total were monitored.

3.1.2 Measurements and analysis

The voltage across an external resistor (1Ω) was recorded every 5 min by a digital multimeter (2700, Keithley Instruments Inc., Cleveland, OH, USA). The current (I) of the BES was calculated with $I = U/R$. The concentrations of chemical oxygen demand (COD), ammonia nitrogen and phosphate were measured using a colorimeter according to the

instructions of the manufacturer (Hach Company, Loveland, CO, USA). Since phosphate measurements using the Low Range Total Phosphate Method in the instructions were not reasonable, thus here the High Range Total Phosphate Method was adopted. The pH and conductivity were measured by a bench top pH meter (Oakton Instruments, Vernon Hills, IL, USA) and a bench-top conductivity meter (Mettler-Toledo, Columbus, OH, USA), respectively.

3.2 Results and Discussions

3.2.1 Nutrients removal over cycles

A concentrating test was operated for 5 consecutive cycles (10 days) in total to understand the maximum recovery capacity and the changes of removal performance over cycles. Notice the digested manure used in this trial had a lower strength in terms of COD, nutrients and conductivity compared to those used in previous studies, because of the variation of digested manure collected from the other lab. Therefore, the performance of the BES was slightly hindered compared to previous results(Fig. 3.1). As shown in Fig. 3.1, the peak current over cycles was 4 mA, 0.5 mA lower than that obtained in the previous study. The current generation also showed a decreasing trend over cycles. This was possibly because of the accumulation of ions in the catholyte that obstructed the ion migration. Lower driving force was also reflected in the removal of nutrients, salinity and COD. According to Fig. 3.2, the removal efficiencies were stable over cycles except phosphate. The average of $\text{NH}_4\text{-N}$, conductivity, COD removal was $59.09\% \pm 1.36\%$, $41.97\% \pm 2.72\%$, $46.45\% \pm 1.57\%$ respectively, less than those removal efficiencies obtained in the previous study. The results showed the key role of current generation in

nutrients removal. Another implication from the anode removal results was that the removal efficiencies were relatively stable over cycles, and the impacts of slightly decreased current generation was not significant. However, these implications only applied to $\text{NH}_4\text{-N}$ but not to $\text{PO}_4\text{-P}$. There was fluctuation in the anode removal of $\text{PO}_4\text{-P}$, further results were needed to testify the pattern.

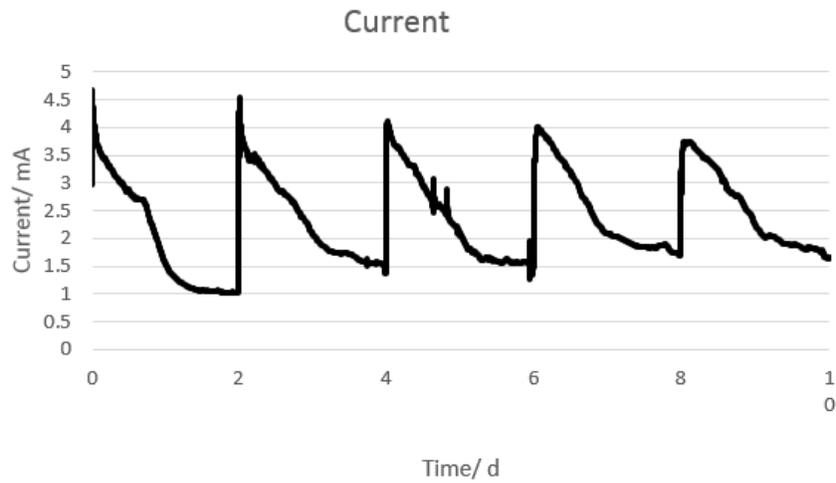


Fig. 3.1 Current generation over cycles

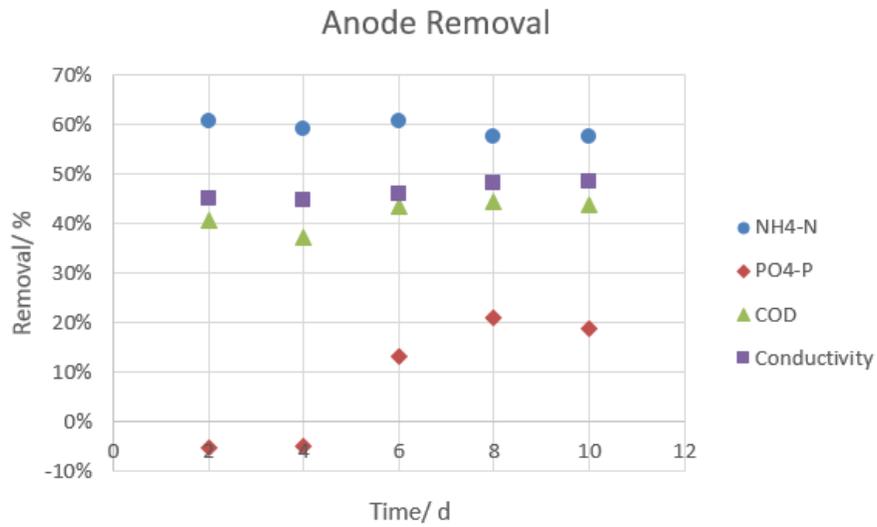


Fig. 3.2 Anode removal over cycles

Although the anode removal showed a stable pattern, the removal in the desalination chamber showed a different trend. As shown in Fig. 3.3, the removal efficiencies of $\text{NH}_4\text{-N}$, conductivity and $\text{PO}_4\text{-P}$ decreased over cycles, but the slopes were different. For $\text{NH}_4\text{-N}$, the removal efficiency decreased from 82.50% to 23.21%, showing a reduction of 72%. For salinity, the removal efficiency decreased from 91.03% to 62.19%, showing a reduction of 32%. For $\text{PO}_4\text{-P}$, the removal efficiency decreased from 66.53% to 31.88%, showing a reduction of 52%. The difference in the slopes were due to different removal mechanisms. The major mechanism of $\text{NH}_4\text{-N}$ and salinity removal was ion migration from low concentration zone to high concentration zone driven by electric field that overcame the concentration gradient. Hence, the main reason for the decrease of both removal efficiencies should be the increase in concentration difference across the membrane over cycles due to the accumulation of ions in the catholyte. Because of the low influent concentration in the desalination chamber, the concentration difference between the desalination chamber and the adjacent chambers was larger than that between the anode chamber and the adjacent chamber. At the beginning of the last cycle of the trial, the concentration of $\text{NH}_4\text{-N}$ in the catholyte was 544.5 mg/L, about twice that in the desalination influent, but 85% of that in the anode influent. The ratio of the concentration difference between the desalination chamber and the adjacent chambers and that between the anode chamber and the adjacent chamber was 2.3. Therefore, it was reasonable that the anode removal showed a stable trend while the desalination removal was decreasing rapidly. The reason why the decrease of $\text{NH}_4\text{-N}$ removal was steeper than that of salinity removal was probably because both cations and anions were able to

migrate through both directions while ammonia could only migrate through the AEM. Hence, under the same driving force, salinity could reach a higher removal compared to $\text{NH}_4\text{-N}$.

It was also demonstrated that phosphate could be removed in the desalination chamber, which was not successfully testified during Section 2. During the first cycle, the $\text{PO}_4\text{-P}$ removal was up to 66.53%. However, compared to the removal of $\text{NH}_4\text{-N}$, the removal of $\text{PO}_4\text{-P}$ was much lower. One of the possibilities was that the migration of phosphate ions was outcompeted by that of other dominant anions such as chloride ions due a smaller charge affinity and a larger hydration diameter during the ion exchange process with hydroxide ions. It was proven by Fei et al. that the presence of chloride ions significant decreased phosphate removal and more phosphate ions could be exchanged at a higher catholyte pH[13]. Another finding was the pattern of the decrease in $\text{PO}_4\text{-P}$ removal over cycles. The removal of $\text{PO}_4\text{-P}$ also showed a decreasing trend over cycles. The increasing anion concentration gradient may be one of the reasons. Since the process also relied on the ion exchange with hydroxide ions, it was possible that the decreasing pH difference between the desalination chamber and the adjacent chambers over cycles impeded the removal of $\text{PO}_4\text{-P}$. A diffusion force that obstructed the migration of hydroxide ions to the desalination chamber was gradually built up, hindering the amount of hydroxide ions transferred to the desalination chamber over cycles.

In terms of COD removal, it was likely accomplished by the metabolism of the remaining microorganisms in the anode effluent and the migration of charged organic molecules

across the ion exchange membrane[54]. However, the COD removal in the desalination chamber was very low compared to the anode chamber and it did not showed a clear pattern of changing over cycles. Thus it was not considered to be an issue in this study.

The total nutrients removal from the digested manure was obtained by adding the removal efficiency in the anode chamber in one cycle to the removal efficiency in the desalination chamber in the subsequent cycle. It was calculated as described above because the effluent from the anode chamber was the influent for the desalination chamber. The hydraulic retention time of the digested manure was 4 days and the effluent from the desalination chamber was the final effluent. The total nutrients removal showed a trend of decreasing over cycles, though not as steep as desalination removal, implying that the anode chamber was a larger contributor to nutrients removal. The final effluent after the desalination chamber will be sent to post treatment unit for further removal of COD and nutrients. By integrating post treatment, the BES can be operated more efficiently. For example, the BES can be stopped at a certain range of COD/N ratio that is suitable for conventional treatment methods. Notice the COD/N ratio in raw digested manure was low, which would bring about difficulties for conventional treatment.

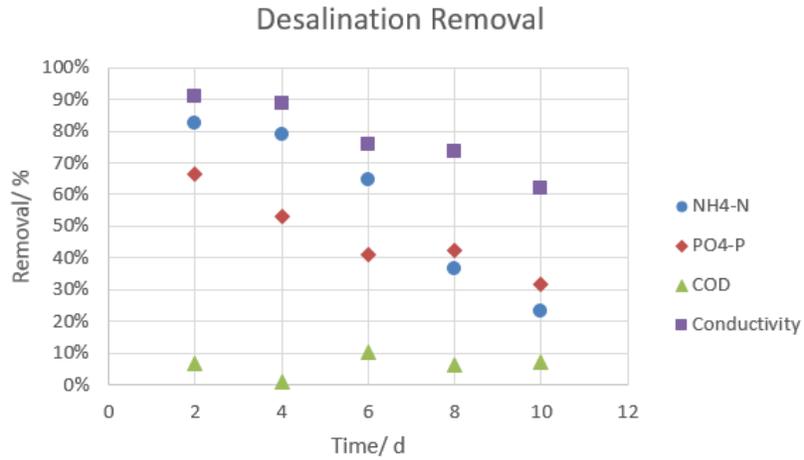


Fig. 3.3 Desalination chamber removal over cycles

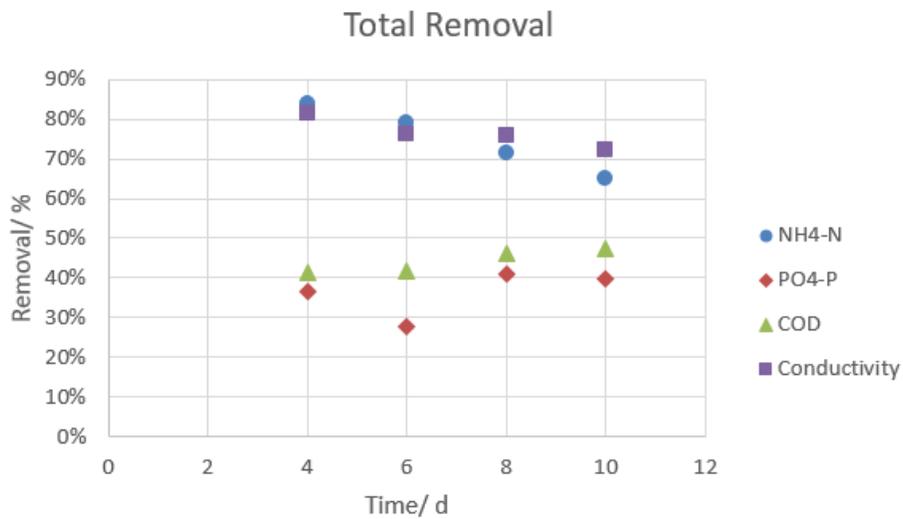


Fig. 3.4 Total removal over cycles

3.2.2 Nutrients recovery over cycles

Although both $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ could be removed by the BES, the recovery of the nutrients did not follow the same pattern as expected. According to Fig. 3.5, there was a significant difference between $\text{NH}_4\text{-N}$ recovery and $\text{PO}_4\text{-P}$ recovery. The catholyte was

able to concentrate $\text{NH}_4\text{-N}$ over cycles, but failed to concentrate $\text{PO}_4\text{-P}$. The concentration of the recovered $\text{NH}_4\text{-N}$ at the end of 5 cycles was up to 670 mg/L (Fig. 3.5), slightly higher than the concentration of $\text{NH}_4\text{-N}$ in raw digested manure as the volume of catholyte was larger than that of the influent for every cycle and a portion of ammonia was lost during the recovering process via other paths. It can also be seen from Fig. 3.5 that the slope of the $\text{NH}_4\text{-N}$ recovery curve showed a slight decrease over cycles, meaning the recovering speed was decreasing slightly over cycles. However, the overall trend is increasing, which suggested that the BES was able to continue to recover $\text{NH}_4\text{-N}$ in further cycles. As discussed in Chapter 3.2.1, the decreased recovering speed could be ascribed to the accumulation of ions in the catholyte, which formed a diffusion gradient to obstruct ion migration. When the nutrient ions accumulated in the recovery chamber, the diffusion of ions driven by increased concentration gradients across membranes partially offset the recovery process[39, 40]. Fig. 3.7 showed that the recovery percentage of $\text{NH}_4\text{-N}$ was stable at a high level of about 55% over cycles. It was much higher than those reported in previous studies, probably because the concentration of $\text{NH}_4\text{-N}$ was much higher in the raw influent in this study, resulting in a relatively smaller portion of $\text{NH}_4\text{-N}$ loss via other paths such as nitrification, biological intake and diffusion into the gas bag. These results demonstrated that the BES was capable of recovering ammonia by concentrating it into the catholyte. In addition, the pH of the catholyte was around 10 over the cycles, providing an effective condition for further recovery of ammonia such as stripping.

The failure of $\text{PO}_4\text{-P}$ recovery was a big issue for the system, since the advantage of the design of the four-chamber BES was to remove and recover both cations and anions simultaneously. Other advantages of the system included the separation of anolyte and other streams so that a suitable environment without other ions flowing in that might inhibit the performance of biofilm was maintained. According to Fig. 3.6, some $\text{PO}_4\text{-P}$ was detected in the catholyte in the beginning. However, the concentration of $\text{PO}_4\text{-P}$ in the catholyte decreased over time and finally was not detected though the $\text{PO}_4\text{-P}$ was removed in the desalination chamber. Based on the assumption that $\text{PO}_4\text{-P}$ migrate across the AEM, it was possible that $\text{PO}_4\text{-P}$ precipitated in the cathode chamber so that the recovery of ionized $\text{PO}_4\text{-P}$ in the solution failed. Previous studies demonstrated the recovery of $\text{PO}_4\text{-P}$ in the catholyte at alkaline conditions, but synthetic municipal wastewater was used without sufficient Mg^{2+} and Ca^{2+} as reservoir for recovery. On the other hand, the digested manure used in this study for nutrients recovery might contain a variety of cations including Mg^{2+} and Ca^{2+} . Although Mg^{2+} and Ca^{2+} measurements were not performed in this study, previous studies on digested manure proved the existence of Mg^{2+} and Ca^{2+} [55]. Considering the possible migration of Mg^{2+} and Ca^{2+} in digested manure to the catholyte, the high ammonia concentration present in the catholyte and the alkaline condition, chemical precipitation of phosphate was likely to occur such as struvite and calcium phosphate.

Phosphate recovery as struvite (also called magnesium ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O}$) is a common practice as struvite exhibits qualities comparable to standard fertilizers[6]. Gadekar and Pullammanappallil indicated two

optimal pH and molar ratio conditions: (1) pH 8.5 at an equimolar mixture of ammonia, magnesium, and phosphate to yield 29% struvite in the solids; and (2) pH 9.8 with a 10:1.7:3.4 molar ratio to yield 98% struvite[56]. Another possible precipitation of phosphate was Calcium-based precipitation in several forms. The most common solid form was calcium phosphate (hydroxyapatite, HAP, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$), which required the presence of Ca^{2+} and high pH (typically over 10)[57]. Given the alkaline condition (pH around 10) in the catholyte, and the presence of sufficient ammonia, Mg^{2+} and Ca^{2+} , it was an ideal environment for chemical precipitation of phosphate, either through struvite precipitation or Calcium-based precipitation. The possibility of Calcium phosphate precipitation was higher since struvite precipitation was in favor of suitable ratio of forming species ($\text{NH}_4^+ : \text{PO}_4^{3-} : \text{Mg}^{2+} = 1 : 1 : 1$), and NH_4^+ was over-sufficient in the catholyte. If chemical precipitation of phosphate happened, the formation of crystal would serve as crystal nucleus that would accelerate the following precipitation process. However, the precipitation of $\text{PO}_4\text{-P}$ could not be verified unless the reactor was dismantled to check if there was crystal on the membrane or on the cathode or in the bottom of the chamber. Dismounting the reactor to check $\text{PO}_4\text{-P}$ precipitation was not performed during in this study, but it should be a step for further investigation.

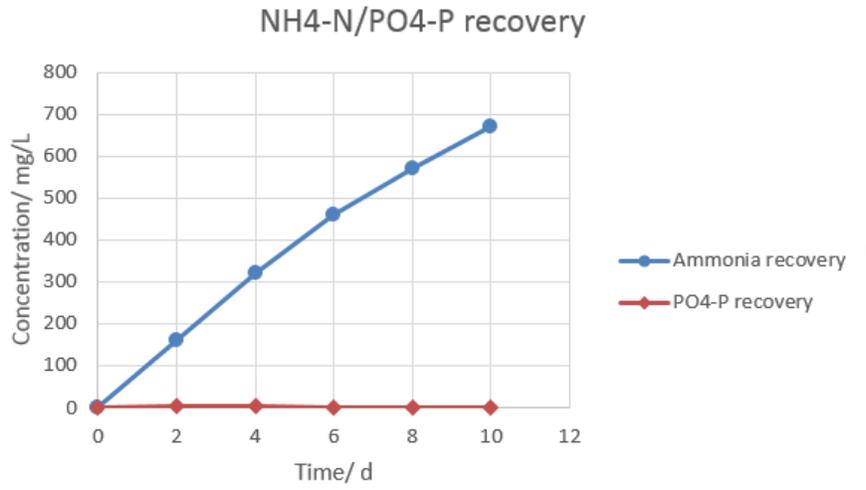


Fig. 3.5 Nutrients recovery over cycles

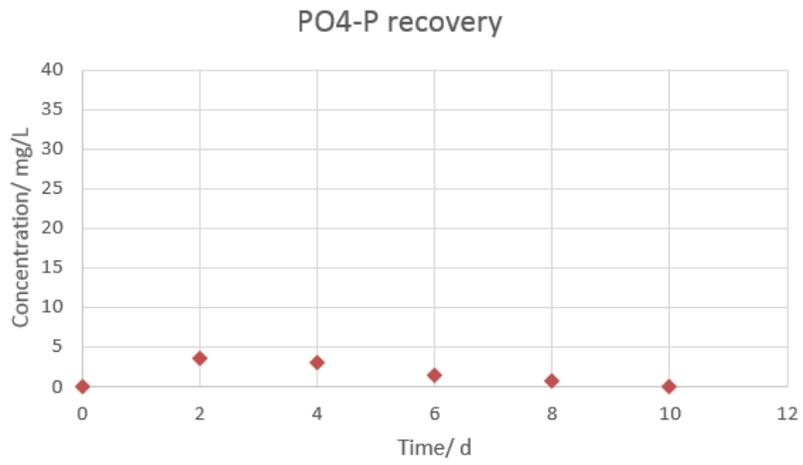


Fig. 3.6 PO₄-P recovery over cycles

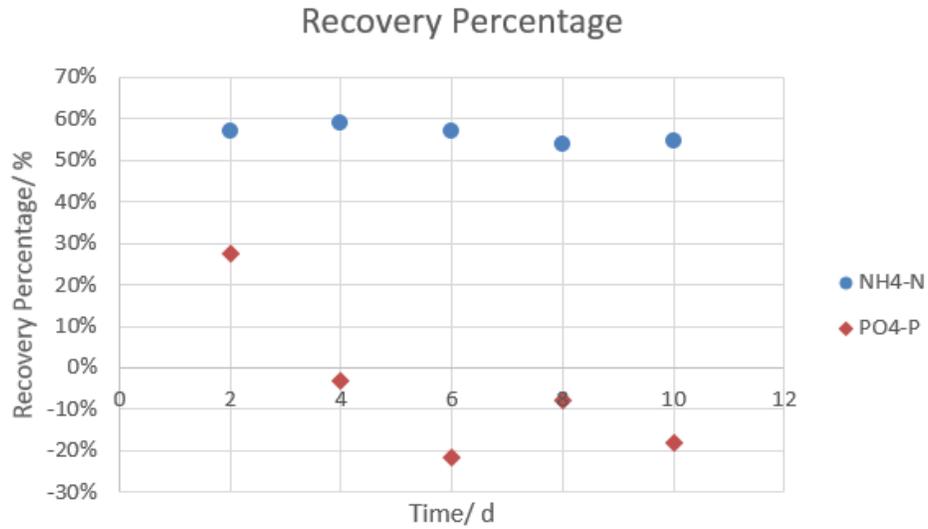


Fig. 3.7 Nutrients recovery percentage over cycles

3.3 Conclusions

The BES demonstrated a high performance of recovering $\text{NH}_4\text{-N}$ in the catholyte in consecutive cycles. The concentration of $\text{NH}_4\text{-N}$ was up to 670 mg/L in the end with a high recovery percentage of 55%. The BES also showed a potential to concentrate $\text{NH}_4\text{-N}$ from digested manure. However, as an important part of nutrients removal and recovery, $\text{PO}_4\text{-P}$ recovery in solution was failed in the BES though $\text{PO}_4\text{-P}$ removal was demonstrated in the system. No $\text{PO}_4\text{-P}$ was detected in the solution at the end of the trial. The possible reason f was that the chemical precipitation of phosphate happened in the catholyte, as the catholyte formed an environment readily for chemical precipitation of phosphate featured with sufficient Mg^{2+} and Ca^{2+} and alkaline condition (pH around 10). The precipitation warrant further studies.

Chapter 4

BES run in different operational conditions

4.1 Materials and Methods

4.1.1 BES Operation

The basic operation of the BES in this trial followed the operation described in Section 3.1.1. The BES were batch-run in consecutive cycles. 60 mL of the anolyte in the external reservoir and 45 mL of the feed for the desalination chamber (anolyte effluent) in the external reservoir were replaced every cycle. The catholyte recirculated between the cathode chamber and the concentration chamber was not replaced in a trial, but 5 mL was sampled and replenished with 1 g·L⁻¹ NaCl solution. The BES was run in different operational conditions to test the changes of the performance. At first, the BES was run with different applied voltage (0.6 V, 0.8 V and 1.0V), each for 3 consecutive cycles, to evaluate the influence of currents on the performance of nutrients removal and recovery. The BES was then run under different hydraulic retention time (HRT, 24, 36 and 48 hours), each condition for 3 consecutive cycles, to explore the impacts of HRT on the performance of nutrients removal and recovery.

4.1.2 Measurements and analysis

The voltage across an external resistor (1Ω) was recorded every 5 min by a digital multimeter (2700, Keithley Instruments Inc., Cleveland, OH, USA). The current (I) of the BES was calculated with $I = U/R$. The concentrations of chemical oxygen demand (COD), ammonia nitrogen and phosphate were measured using a colorimeter according to the instructions of the manufacturer (Hach Company, Loveland, CO, USA). Since phosphate

measurements using the Low Range Total Phosphate Method in the instructions were not reasonable, thus here the High Range Total Phosphate Method was adopted. The pH and conductivity were measured by a bench top pH meter (Oakton Instruments, Vernon Hills, IL, USA) and a bench-top conductivity meter (Mettler-Toledo, Columbus, OH, USA), respectively.

4.2 Results and Discussions

4.2.1 BES performance with different applied voltages

The BES was run with different applied voltages of 0.6 V, 0.8 V and 1.0 V to test the influence of current on the performance of nutrients removal and recovery. It was expected that there was a linear relationship between the applied voltage and the current generation. However, according to Fig. 4.1, the current generation under different voltages showed a different pattern. It was seen from Fig. 4.1 that the average current generation under 0.8 V was significantly higher than that under 0.6 V. The peak current obtained under 1.0 V was higher than that under 0.8 V. When looking at the average current generation during the whole cycles, there was no significant difference between the current generation under 0.8 V and 1.0 V, so did the average electric driving force under two conditions. The reason why there was no significant difference was not clear.

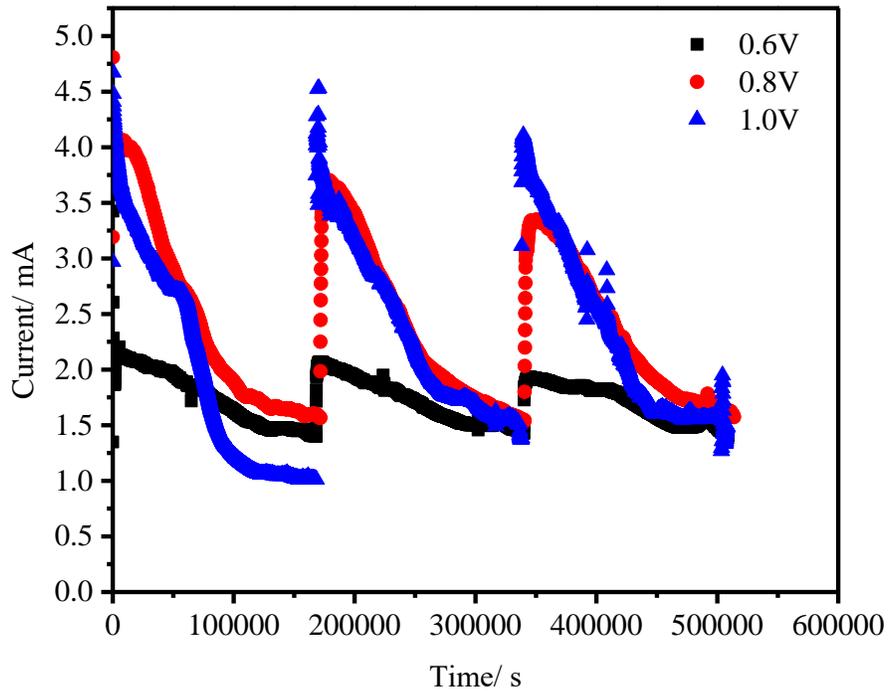


Fig. 4.1 Current generation with different applied voltages

Previous results of the ammonia recovery and total ammonia removal demonstrated that the stronger the electric driving force, the more $\text{NH}_4\text{-N}$ removed and recovered from digested manure. First look at the ammonia recovery in the catholyte during 3 cycles shown in Fig. 4.2, there was a significant difference between the concentration of recovered $\text{NH}_4\text{-N}$ in the catholyte under 0.6 V and 0.8 V. At the end of all three cycles, the concentrated $\text{NH}_4\text{-N}$ under 0.6 V was $290 \text{ mg}\cdot\text{L}^{-1}$, while that under 0.8 V and 1.0 V was $460 \text{ mg}\cdot\text{L}^{-1}$ and $500 \text{ mg}\cdot\text{L}^{-1}$ respectively. The ratio of the absolute mass of recovered $\text{NH}_4\text{-N}$ under 0.8 V to that under 0.6 V was about 1.6. The similar pattern was found in the removal efficiencies. According to Fig. 4.3, $\text{NH}_4\text{-N}$ removal under 0.8 V was significantly higher than that under 0.6 V. However, the difference of ammonia removal

was not as large as that of ammonia recovery, which could be attributed to the difference between the recover percentages under different applied voltages. When 0.8 V was applied to the BES, the average recover percentage was 58.40%, while the average recover percentage was 43.47% under 0.6 V. The results explained the larger difference present in the ammonia recovery and indicated that the higher the current generation, the higher percentage of $\text{NH}_4\text{-N}$ could be recovered into the catholyte.

However, when it came to the comparison of the ammonia removal and recovery between 0.8 V and 1.0 V, contradictory results were found from Fig. 4.2 and Fig. 4.3. Under 1.0 V, the concentration of $\text{NH}_4\text{-N}$ recovered in the catholyte was slightly higher than that under 0.8 V. Although Fig. 4.1 did not showed a clear difference between average current generation of the BES under 0.8 V and 1.0 V, the calculated average current generation under 1.0 V was slightly higher than that under 0.8 V (2.4 mA vs. 2.3 mA). However, the total $\text{NH}_4\text{-N}$ removal under 1.0 V was slightly lower than that under 0.8 V (Fig. 4.3). The results did not seem to make sense as the total $\text{NH}_4\text{-N}$ removal should be slightly higher according to the average current generation. Looking at the recover percentage obtained under different conditions, the average recover percentage obtained under 0.8 V was 58.40%, while the average recover percentage obtained under 1.0 V was 62.25%. One possible reason was that the calculated removal of $\text{NH}_4\text{-N}$ came from two parts, ion migration across the CEM and dilution at the beginning of a cycle. Dilution of influent happened because only the solutions in the external reservoirs were replaced every cycle. Hence, the remaining solution inside the chambers with low concentration resulted from $\text{NH}_4\text{-N}$ removal in the last cycle was able to dilute the influent at first. In this case, the

cycles run under 1.0 V were started right after the cycles run under 0.6 V. Therefore, the remaining solutions in the chambers during the initial cycle under 1.0 V had higher ammonia concentration than the remaining solutions during the initial cycle under 0.8 V. As result, the effect of dilution on $\text{NH}_4\text{-N}$ removal in 1.0 V cycles was weaker than that in 0.8 V cycles. Hence, it was reasonable that ammonia recovery during 1.0 V cycles was slightly higher than that in 0.8 V cycles but ammonia removal was slightly lower.

For phosphate removal, the results did not show a trend corresponding to current generation (Fig. 4.4). Rather, it showed fluctuation of phosphate removal. Moreover, the figure showed that the average phosphate removal were enhanced with longer operation. This was likely because there were more crystal nucleus formed in the later cycles, leading to accelerated chemical precipitation of phosphate in the desalination chamber. This could be true since at the end of every cycle under 0.6 V and 1.0 V, no $\text{PO}_4\text{-P}$ was detected in the catholyte, and it could be due to the accelerated chemical precipitation of phosphate caused by accumulated crystal nucleus in the cathode chamber and concentration chamber. The finding could probably also help to explain the loss of $\text{PO}_4\text{-P}$ in the catholyte, as amendment to previous reasoning.

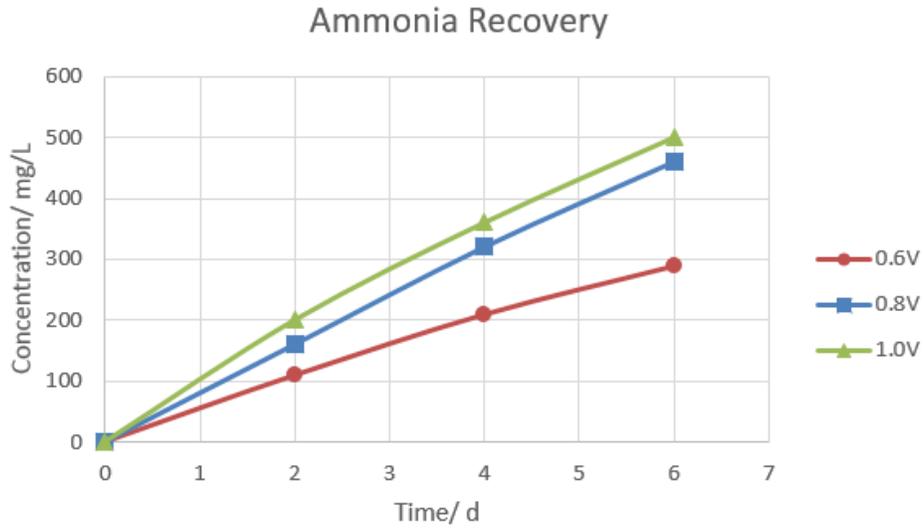


Fig. 4.2 Ammonia recovery with different applied voltages

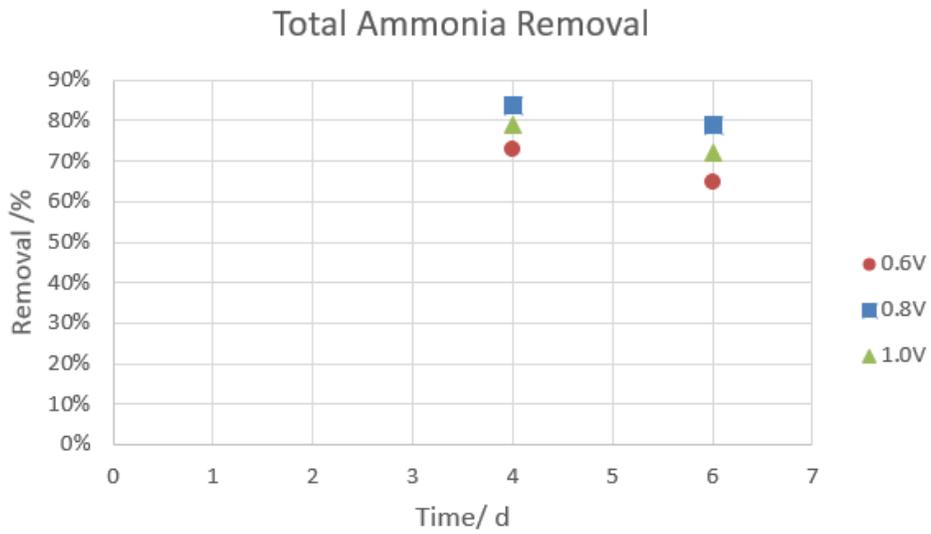


Fig. 4.3 Total ammonia removal with different applied voltages

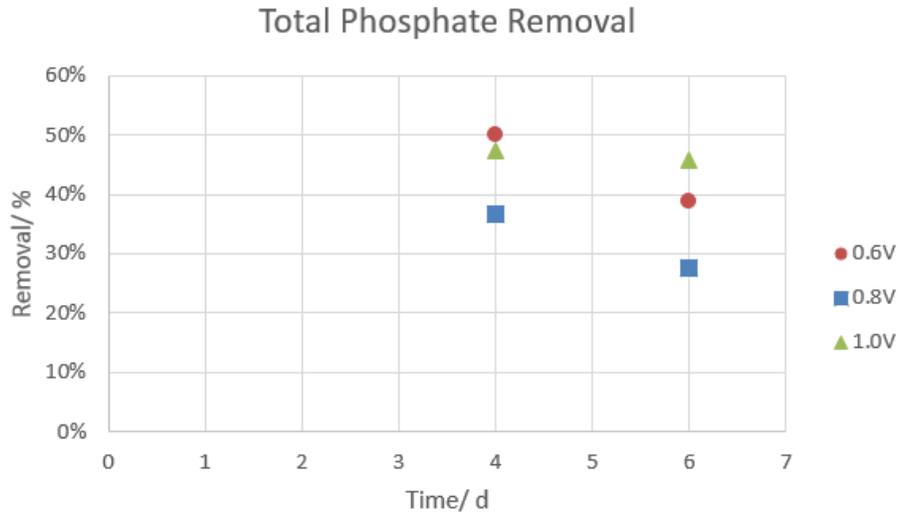


Fig. 4.4 Total phosphate removal with different applied voltages

4.2.2 BES performance with different HRT

The BES was run under a series of different HRTs (24, 36 and 48 hours) with the same applied voltage of 1 V to test the influence of HRT on nutrients removal and recovery and to understand the distribution of nutrients removal and recovery over time. The results showed that there was no distinct difference in nutrients removal and recover at different HRTs. As shown in Fig. 4.5, at the end of 3 consecutive cycles, the concentration of recovered ammonia in the catholyte was 500 mg/L, 460 mg/L and 430 mg/L, respectively under the HRT of 48 hours, 36 hours and 24 hours. The same pattern was also found in the total removal of ammonia (Fig. 4.6). These results indicated that most of the $\text{NH}_4\text{-N}$ was removed and recovered during the first 24 hours, during which the current generation was high. In contrast, few $\text{NH}_4\text{-N}$ was removed and recovered in the low current generation period during one cycle, which should be considered when determining the suitable HRT for the BES integrated with post treatment. The result was also a demonstration of the key role of electric driving force in ammonia removal and

recovery in the BES. In terms of $\text{PO}_4\text{-P}$ removal (Fig. 4.7), no significant difference in different HRT was observed, showing a similar pattern with $\text{NH}_4\text{-N}$ removal. A possible indication from the result was that the current generation was a key factor in $\text{PO}_4\text{-P}$ removal, most of which were accomplished under high current. Another phenomenon that was worth notifying was that at the end of every cycle, no $\text{PO}_4\text{-P}$ was detected in the catholyte. Notice that during the trial described in Section 3, a low concentration of $\text{PO}_4\text{-P}$ was detected in the catholyte. This phenomenon probably meant that the chemical precipitation of phosphate was accelerated, and it could be true since crystal nucleus formed during previous cycles which would accelerate the chemical reactions. If this hypothesis holds true, the BES can be a good approach to recover $\text{PO}_4\text{-P}$ as crystal instead of ions in solution.

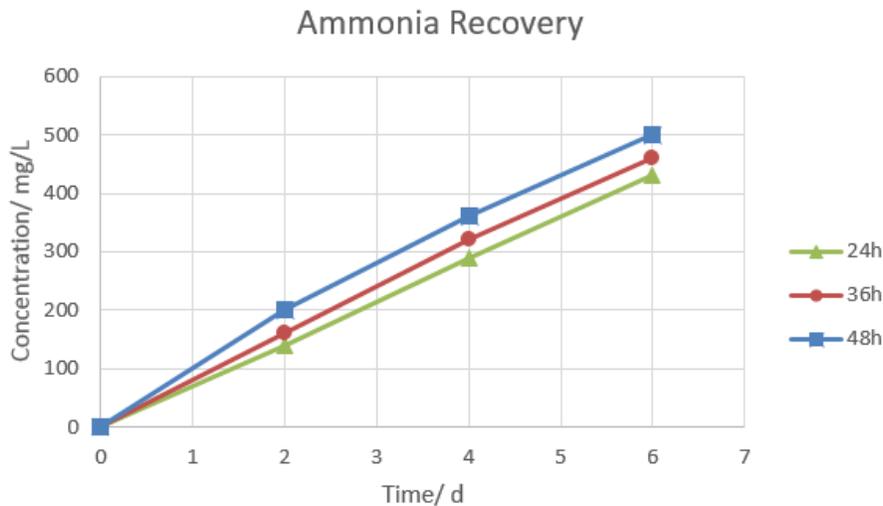


Fig. 4.5 Ammonia recovery with different HRT

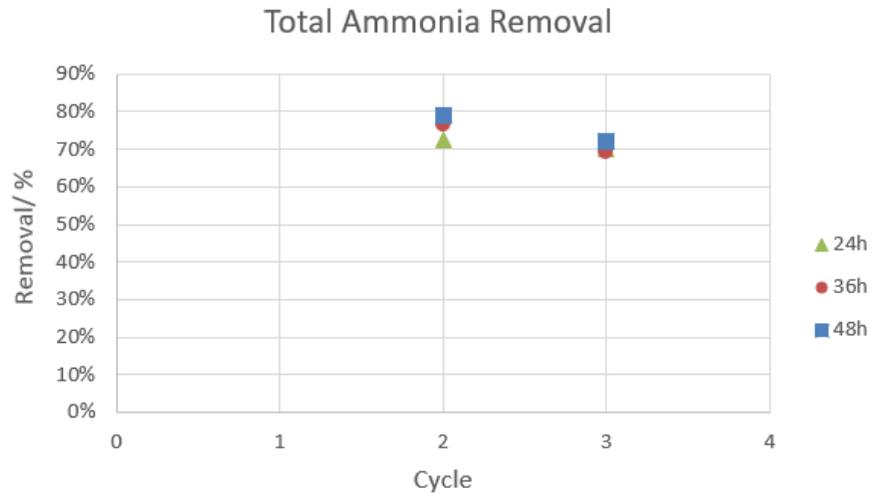


Fig. 4.6 Ammonia removal with different HRT

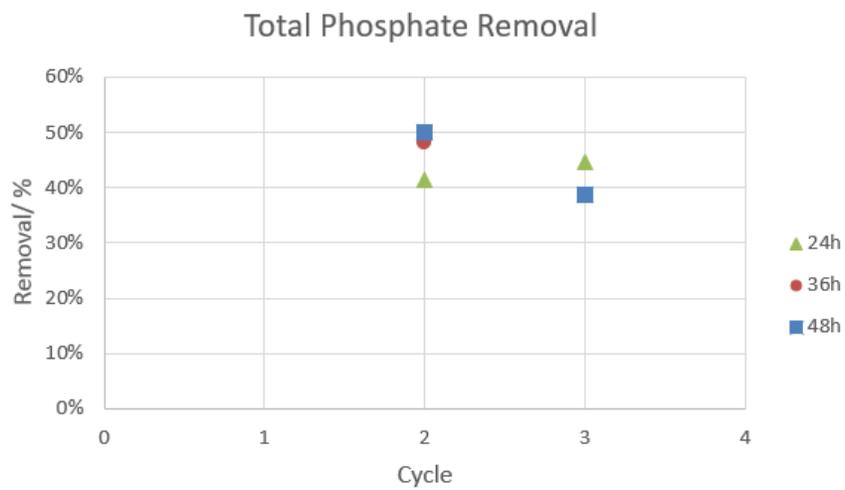


Fig. 4.7 Phosphate removal with different HRT

4.3 Conclusions

The BES was run under different applied voltage and HRT. The results showed that the BES achieved a higher performance at higher applied voltages. However, the BES under

the applied voltage of 0.8 V and 1.0 V did not show much difference in current generation, nutrients removal and recovery, indicating a low energy efficiency when applied voltage was higher than 0.8 V. The results under different HRT showed that there was no noticeable difference in the performance. The phenomenon revealed that most of the nutrient removal and recovery was completed during high current stage in a cycle within 24 hours. The result also demonstrated the key role of current generation in nutrient removal and recovery. These findings provided necessary information for the determination of suitable operational conditions in further study of the BES, especially when post treatment of the effluent was integrated.

Chapter 5

Perspectives

The removal and recovery of Cr(VI), ammonia and phosphate by the four-chamber BES was investigated in this study. The BES was able to remove Cr(VI) nearly completely from the desalination chamber in a 5-day cycle, but failed to recover any Cr(VI). It was demonstrated that the Cr(VI) was mainly removed by membrane adsorption instead of ion migration across the membrane, as polychromate would first form in the membrane then transport chromate ions across the membrane.

The performance of the BES was evaluated and the feasibility of using the BES to remove and recover nutrients from digested manure was investigated. The BES achieved a high performance in terms of current generation and desalination in a 48-hour cycle either under the MFC mode or the MEC mode, indicating the design of the BES featured with high ratio of membrane area to chamber volume and high COD input for the anode had a high potential in nutrients removal and recovery. Subsequent studies in a single cycle demonstrated the feasibility of nutrient removal and recovery. The removal efficiency reached 86% for NH₄-N and 50% for COD removal in a single cycle. A high recovery of NH₄-N (up to 60%) was achieved, indicating the key role of current generation in NH₄-N removal and recovery. PO₄-P removal and recovery was not well evaluated in due to the ineffective PO₄-P measurements using an inappropriate method.

Nutrient removal and recovery from digested manure in consecutive cycles was explored to find out maximum treat capacity of the BES. It was demonstrated that the BES was

able to recover 670 mg/L of $\text{NH}_4\text{-N}$ in 5 cycles in the catholyte and the slowly decreased recovering speed showed the potential to continue to recover. The contribution of the anode removal was much larger than that of desalination chamber removal, resulting in a slight change of removal in anode but rapidly decreased removal in the desalination chamber due to increased concentration gradient built as ions accumulated in the catholyte. The BES was able to achieve $\text{PO}_4\text{-P}$ removal in the desalination chamber and it also showed a decreasing trend. However, the BES failed to recover $\text{PO}_4\text{-P}$ in solution, probably due to chemical precipitation such as struvite or Ca-based precipitation. The alkaline condition and cations such as Mg^{2+} and Ca^{2+} could create an environment that favored phosphate precipitation.

Finally, the BES was tested under different applied voltage and HRT. It was demonstrated that higher current generation led to higher nutrients removal and recovery, again indicating the key role of electric driving force in nutrients removal and recovery. It was also demonstrated that most of the nutrients were removed and recovered during the high current stage in a cycle within 24 hours. These findings can help us better understand of the mechanism of nutrients removal and recovery in the BES and can be useful for determining the operational conditions in further study.

The four-chamber BES has been demonstrated effective and efficient in nutrients removal and $\text{NH}_4\text{-N}$ recovery. However, $\text{PO}_4\text{-P}$ recovery remained a question that needed to be studied in the future. Future work would focus on phosphate precipitation on the membrane and the cathode by dismounting the reactor. If phosphate precipitation was

verified, a strategy of recovering $\text{PO}_4\text{-P}$ would be developed in the future. Digested manure without $\text{PO}_4\text{-P}$ pretreatment might be a better source for the BES. Further recovery of excess $\text{NH}_4\text{-N}$ such as stripping should also be investigated. Post treatment of the effluent would also be integrated and suitable operational conditions would be examined to optimize the system efficiency. A combined strategy capable of treating digested manure and reclaiming nutrients and energy would be developed using the BES in the study in the future.

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