Ammonium Removal from Synthetic Wastewater Promoted by Current Generation and Water Flux in an Osmotic Microbial Fuel Cell

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Abstract

Recovering useful resource from wastes represents a new approach of clean production with significant environmental and economic benefits. Ammonium nitrogen, which is an important inorganic contaminant and also a resource for fertilizer, can be removed and recovered from wastewater. As the first step of recovery, ammonium removal was successfully demonstrated in this study by using an innovative treatment system - osmotic microbial fuel cells (OsMFC). This OsMFC achieved the removal efficiency of $80.1 \pm 2.0 \%$ with an anolyte flow rate of 0.4 mL min^{-1} . Current generation was a key driving force for ammonium ion movement and increasing current generation from 0 to $1.8 \pm 0.1 \text{ A m}^{-2}$ could greatly enhance the removal efficiency from $40.7 \pm 2.4 \%$ to $85.3 \pm 3.5 \%$. When current generation was similar, water flux could contribute significantly to facilitating ammonium removal, and as a result the OsMFC exhibited $55.2 \pm 6.5 \%$ higher ammonium removal with water flux of $1.3 \pm 0.2 \text{ LMH}$ than that without water flux. In addition, ion diffusion and ion exchange contributed to $17.3 \pm 2.4 \%$ and $2.8 \pm 0.1 \%$ of ammonium removal, respectively, with $35 \text{ g L}^{-1} \text{ NaCl}$ as a catholyte. The key challenges such as the exact mechanism of ammonium transport, disposal of ammonium residue after recovery, effects of draw solutes, and system scaling up have been identified and discussed. The results of this study will help develop an efficient approach for NEW recovery (NEW: nutrient, energy and water) from wastewater.

Keywords: Osmotic microbial fuel cells; forward osmosis; ammonium removal and recovery; current generation; water flux.

1. INTRODUCTION

Nitrogen removal from wastewater is of great importance to protect receiving water from eutrophication (Matassa et al., 2015). The primary form of nitrogen in wastewater is ammonia (Sprynskyy et al., 2005), which can be biologically converted to nitrogen gas via nitrification and denitrification, or anaerobic ammonium oxidation (anammox) (Ahn, 2006; Gupta et al., 2015). Significant energy/chemical input is required by biological nitrogen removal. Meanwhile, ammonia nitrogen is a key fertilizer component for agricultural production, and more than 90% of the world ammonia is produced by using the Haber-Bosch synthesis process, which consumes 1-2% of the world energy to synthesize ammonia from hydrogen gas and nitrogen gas under a high pressure (Bicer et al., 2016). Therefore, both the need for ammonia removal from wastewater and the high energy demand for synthesizing ammonia stimulate the interest in recovering ammonia from wastewater, instead of removal, and such recovery will synergistically address the nexus of food, energy, and water.

Ammonia can be recovered from wastewater by using an emerging technology - microbial fuel cells (MFCs) (Arredondo et al., 2015; Kelly and He, 2014). In MFCs, organic compounds in wastewater are oxidized by the exoelectrogens growing on an anode electrode and the generated electrons can spontaneously flow from the anode electrode to a cathode electrode for electricity generation (Li et al., 2014). Electron flow will drive transport of ions between the anode and the cathode to keep electroneutrality, depending on the types of ion exchange membrane used in an MFC. When cation exchange membrane (CEM) is used, cations such as protons, sodium ions and ammonium ions will migrate from the anode into the cathode. As a result of cathode reduction reaction, the pH of the catholyte could increase to above 11-12, which will facilitate

conversion of ammonium to ammonia for subsequent recovery by stripping. Ammonia recovery by MFCs has been successfully demonstrated in laboratory studies (Kuntke et al., 2011), and higher current generation would greatly enhance the ammonia recovery (Haddadi et al., 2013; Kuntke et al., 2014). Ammonia can be recovered from various types of ammonium-rich wastewater, such as urine, landfill leachate, and swine wastewater (Kim et al., 2008; Kuntke et al., 2011; Kuntke et al., 2012; Qin et al., 2016b; Zhang et al., 2014).

To enhance water recovery in MFCs, osmotic microbial fuel cells (OsMFCs) were developed through integrating forward osmosis (FO) with MFCs (Lu et al., 2014b; Zhang et al., 2011). In OsMFCs, FO membrane instead of CEM is used to separate the anode and the cathode and this semipermeable membrane only permeates water molecules from high water potential to low water potential driven by an osmotic pressure gradient (Cath et al., 2006). Like conventional MFCs, electricity is generated from the oxidation of organics by exoelectrogens in an anode and a terminal electron acceptor such as oxygen is reduced on a cathode catalyzed by catalysts. The difference from conventional MFCs is that OsMFCs can extract high quality water from the anolyte (e.g., wastewater) by using FO membrane. In addition, OsMFCs can generate more electricity under both a batch mode and a continuous mode using either sodium chloride solution or artificial seawater as the catholyte (Ge et al., 2013; Zhang et al., 2011). More than 50% of the treated wastewater could be extracted from the anode of an OsMFC (Ge et al., 2013; Ismail and Ibrahim, 2015). To improve our understanding of enhanced electricity generation in OsMFCs, a mathematical model has been developed and used to predict a reduction of internal resistance with increasing osmotic pressure gradient and water flux, thereby confirming the enhanced current generation (Qin et al., 2015). It was also reported that in an OsMFC, reverse salt flux

(RSF), which is backward transport of salt ions across the FO membrane into the treated wastewater, was significantly inhibited by the current generation (Qin et al., 2016a).

Higher current generation in OsMFCs encourages the exploration of recovering ammonia, which relies on ammonium transport driven by current generation. The past OsMFC studies focus on recovery of resources such as electricity and water, but ammonia recovery in OsMFCs has not been investigated. Unlike CEM, FO membrane cannot selectively transport ions. However, the unique feature of OsMFCs, water flux, has been found to help improve current generation. Therefore, it will be of great interest to accomplish ammonia recovery in OsMFCs, making OsMFCs a promising technology for “NEW recovery” (NEW: nutrient, energy and water). In this study, we have investigated ammonium removal in a laboratory OsMFC towards understanding of the effects of current generation and water flux on ammonia removal. The recovery of ammonia gas was beyond the scope of this work but it has been performed in various studies via highly efficient absorption in acids (Kuntke et al., 2012; Liu et al., 2016; Wu and Modin, 2013). The specific objectives were to: (1) demonstrate the feasibility of ammonium removal in an OsMFC; (2) investigate the effect of the current generation and water flux on ammonium removal; and (3) explore the mechanism of ammonium removal in the OsMFC.

2. MATERIALS AND METHODS

2.1 OsMFC setup

The OsMFC consisted of two equal-size compartments ($14 \times 7 \times 3.7$ cm³/each with a liquid volume of 280 mL) as the anode and the cathode, respectively, separated by a TFC FO membrane (Hydration Technology Innovations, LLC, Albany, OR, USA) with its active layer facing the

anode (feed) side. Plastic mesh was placed on both sides of the FO membrane as support materials. Two carbon brushes (Gordon Brush Mfg. Co. Inc., Commerce, CA, USA) were pretreated by being soaked in pure acetone overnight and heat-treated in a muffle furnace (Model 550 Isotemp Series, Fisher Scientific, Pittsburgh, PA, USA) at 450 °C for 30 minutes; after pretreatment they were inserted into the anode compartment as the anode electrodes. The cathode electrode was a piece of carbon cloth coated with Platinum (Pt) as the catalyst for oxygen reduction reaction ($0.3 \text{ mg Pt cm}^{-2}$). Before use, the TFC membrane was soaked in deionized (DI) water for 30 min according to the manufacturer's instruction (Stillman et al., 2014). The surface area of the FO membrane was about 98 cm^2 .

2.2 OsMFC operation

The OsMFC was operated at room temperature of $\sim 21^\circ\text{C}$. The anode compartment was inoculated with anaerobic sludge from the Peppers Ferry Regional Wastewater Treatment Plant (Radford, VA, USA). To mimic the digestion effluent of livestock waste (Park et al., 2010), the anode influent solution was prepared containing (per liter of deionized water): sodium acetate, 1.5 g; NH_4Cl , 3.0 g; NaHCO_3 , 2.0 g; NaCl , 0.15 g; MgSO_4 , 0.005 g; CaCl_2 , 0.006 g; and trace elements solution, 1 mL (Angenent and Sung, 2001). The initial concentration of COD in the anode influent was 1200 mg L^{-1} while the initial concentration of ammonium nitrogen ($\text{NH}_4^+\text{-N}$) was 780 mg L^{-1} . Sodium chloride was used as the draw solute for water extraction. To avoid the difference in performance caused by reactor manufacturing, the same OsMFC reactor was used for all the tests. The OsMFC was operated in a continuous mode. The 2-L bottles were connected to the anode and cathode compartments as reservoirs and placed on digital balance for monitoring water flux. The cathode compartment was aerated with the air to provide oxygen for

cathode reaction and create flow turbulence. To study the effects of current generation, the external resistance was adjusted to four levels (10 Ω , 20 Ω , 40 Ω and quasi-infinite or open circuit mode), and the catholyte was 35 g L⁻¹ NaCl. In the experiments of different water flux, the concentration of the draw solution (catholyte) was varied at 2 g L⁻¹, 10 g L⁻¹ and 35 g L⁻¹. The effect of the anolyte flow rate on ammonium removal was investigated with 35 g L⁻¹ NaCl as the catholyte at different flow rates: 0.2 mL min⁻¹, 0.3 mL min⁻¹ and 0.4 mL min⁻¹. The effect of water flux on ammonium removal was examined in both closed-circuit condition and open-circuit condition with different catholyte NaCl concentrations (2 g L⁻¹ and 35 g L⁻¹). The ammonium removal with different water flux and same current generation was studied with two operations: (1) 2 g L⁻¹ NaCl catholyte and 10 Ω external resistor; and (2) 35 g L⁻¹ NaCl catholyte and 88 Ω resistor. The ammonium transported to the cathode side could be recovered as ammonia gas, which has been demonstrated in our previous studies (Liu et al., 2016; Qin and He, 2014). The present study focused on the ammonium removal, and the recovery was not performed.

2.3 Measurement and analysis

The OsMFC voltage was recorded every 2 minutes by a digital multimeter (2700, Keithley Instruments Inc., Cleveland, OH, USA). The polarization curve was performed by using a potentiostat (Reference 600, Gamry Instruments, Warminster, PA, USA) at a scan rate of 0.2 mV s⁻¹. The pH was measured by using a benchtop pH meter (Oakton Instruments, Vernon Hills, IL, USA). The conductivity was measured by using a benchtop conductivity meter (Mettler-Toledo, Columbus, OH, USA). The volumetric densities of power and current were calculated based on the liquid volume of the anode compartment, according to a previous study (Zhang et al., 2010).

The concentrations of chemical oxygen demand (COD) and ammonium nitrogen ($\text{NH}_4^+\text{-N}$) were measured using a DR/890 colorimeter (HACH Co., Ltd., USA) according to the manufacturer's instruction. The catholyte weight in the reservoir was recorded every 1 min on a digital balance (Scort Pro, Ohous, Columbia, MD, USA) (Zou and He, 2016). The concentrations of Na^+ and Cl^- were quantified by using ion chromatography (Dionex LC20 ion chromatograph, Sunnyvale, CA, U.S.A.) equipped with an ED40 electrochemical detector. The COD removal efficiency ($\text{COD}_{\text{Removal}}$) was calculated as:

$$\text{COD}_{\text{Removal}} = 1 - \frac{C_{\text{effluent}} \times Q_{\text{effluent}}}{C_{\text{influent}} \times Q_{\text{influent}}} \quad (\text{Eq. 1})$$

where C_{effluent} and C_{influent} are the COD for effluent and influent (mol L^{-1}), respectively. Q_{effluent} and Q_{influent} are the flow rate of anode effluent and anode influent (L min^{-1}), respectively.

Water flux J_w across the FO membrane ($\text{L m}^{-2} \text{h}^{-1}$, LMH) was calculated by the weight change of catholyte solution over time (Wang et al., 2010).

$$J_w = \frac{V_{c,t} - V_{c,0}}{A_m t} \quad (\text{Eq. 2})$$

where $V_{c,t}$ and $V_{c,0}$ are the volume (L) of the catholyte at the test time t (h) and 0, respectively.

The difference between $V_{c,t}$ and $V_{c,0}$ equals to the weight increase of the draw solution in value (kg) during this period; A_m is the membrane area (m^2).

3. RESULTS AND DISCUSSION

3.1 Feasibility of Ammonium Removal across FO Membrane

To examine the feasibility of ammonium removal, the OsMFC was operated with varied NaCl concentrations in the catholyte. Current density increased from $1.1 \pm 0.1 \text{ A m}^{-2}$ to $2.6 \pm 0.1 \text{ A m}^{-2}$

(mean value $\pm$ standard deviation) when the NaCl concentration increased from 2 g L⁻¹ to 35 g L⁻¹ (Fig. 1A). Both the membrane resistance and catholyte resistance are related to the reciprocal of catholyte solution conductivity (Qin et al., 2015). A higher NaCl concentration could increase the catholyte conductivity and decrease both the membrane resistance and catholyte resistance, thereby increasing current generation. In addition, the OsMFC with 35 g L⁻¹ NaCl had a higher COD removal efficiency (80.7 ± 1.5 %) than that with 2 g L⁻¹ NaCl (64.7 ± 1.9 %), benefited from the higher current generation. The ammonium removal efficiency was 23.5 ± 3.5 %, 34.3 ± 5.3 %, and 52.5 ± 4.7 %, with 2, 10, and 35 g L⁻¹, respectively (Fig. 1B). When the catholyte NaCl concentration was 2 g L⁻¹, there was no water flux (0 ± 0.1 LMH) (Fig. 1B). As the increase of catholyte NaCl concentration, the osmotic pressure difference ($\Delta \pi$, calculated from the salt concentration in two chambers) between the anode (feed) and the cathode (draw) increased and therefore, the water flux from anode to the cathode increased to 0.7 ± 0.1 LMH and 1.3 ± 0.2 LMH with a NaCl concentration of 10 g L⁻¹ and 35 g L⁻¹, respectively. Such an increase in water flux would help with ammonium removal, which will be discussed in the following sections

3.2 Effects of Anolyte Flow Rate

The anolyte flow rate is a key operating factor and could affect the loading rates of both organic compounds and ammonium. When the anolyte flow rate was 0.2 mL min⁻¹, 0.3 mL min⁻¹ and 0.4 mL min⁻¹, the ammonium loading rate was 0.5, 1.0, and 1.5 mmol h⁻¹, respectively. During the test, the catholyte NaCl concentration was maintained at 35 g L⁻¹. Varying the anolyte flow rate also changed organic input, resulting in increased current generation with a higher flow rate. For example, current density increased from 1.8 ± 0.1 to 2.6 ± 0.1 A m⁻², when the anolyte flow rate

was changed from 0.2 to 0.4 mL min⁻¹ (Fig. 2A). However, the COD removal efficiency decreased as the anolyte flow rate increased: $91.3 \pm 2.3 \%$, $85.2 \pm 1.1 \%$, and $80.7 \pm 1.5 \%$ with three flow rates. The ammonium removal efficiency was clearly affected by the anolyte flow rate. Increasing the anolyte flow rate from 0.2 to 0.4 mL min⁻¹ decreased the ammonium removal efficiency from $85.3 \pm 3.5 \%$ to $52.5 \pm 4.7 \%$ (Fig. 2A). Assuming one electron generated from the oxidation of organic substrates in the anode moves one ammonium ion from the anode into the cathode for charge balance, the transport of ammonium ions would contribute to $69.3 \pm 1.9 \%$, $78.0 \pm 3.1 \%$, and $80.1 \pm 2.0 \%$ of ionic flux through the FO membrane with the anolyte flow rate of 0.2, 0.3 and 0.4 mL min⁻¹, respectively. Thus, a higher anolyte flow rate would improve the importance of ammonium ions as a proton shuttle in the OsMFC (Cord-Ruwisch et al., 2011). Water flux was not changed significantly with varied anolyte flow rates ($p > 0.05$, Fig. 2B), likely due to the small change in osmotic pressure difference under those conditions.

3.3 Effects of Current Generation

Current generation (or electron flow) is a key driving force for ammonium transport, and its importance in the OsMFC was examined under the conditions of varied external resistance. When applying a 10 Ω external resistor and 35 g L⁻¹ NaCl as the catholyte, current density was $1.8 \pm 0.1 \text{ A m}^{-2}$ (Fig. 3A), and the ammonium removal efficiency was $85.3 \pm 3.5 \%$ (Fig. 3B). For comparison, the OsMFC under the open-circuit condition did not generate any current and removed $40.7 \pm 2.4 \%$ of ammonium nitrogen (Fig. 3B). Further comparison was conducted with 2 g L⁻¹ NaCl as the catholyte, which led to no water flux due to the lack of osmotic pressure gradient. Likewise, current generation, although lower at $0.8 \pm 0.1 \text{ A m}^{-2}$ than that with 35 g L⁻¹ catholyte, increased the ammonium removal efficiency from $21.4 \pm 2.2 \%$ (open circuit condition)

to $47.8 \pm 2.2 \%$ (Fig. 3B). Those results have confirmed the critical role of current generation in driving ammonium ions out of the anolyte and moving through the FO membrane. In addition to current-driven movement, ammonium ions could also migrate due to the ammonium concentration gradient and ion exchange, which resulted in ammonium removal under the open circuit condition.

More external resistances were examined to reveal the relationship between ammonium removal and current generation in the OsMFC. This was investigated at a fixed ammonium loading rate of 0.5 mmol h^{-1} and fixed catholyte NaCl concentration of 35 g L^{-1} . As shown in the polarization curve (Fig. 3C), the open circuit voltage of the OsMFC was 0.78 V with an estimated internal resistance of 19.2Ω . Therefore, the external resistance was varied from 10Ω to 40Ω to represent different current generation including the condition of the maximum power output. As expected, current density increased from $1.0 \pm 0.1 \text{ A m}^{-2}$ to $1.8 \pm 0.1 \text{ A m}^{-2}$ when the external resistance decreased from 40Ω to 10Ω (Fig. 3D). Ammonium removal clearly increased from $60.5 \pm 3.9 \%$ (40Ω) to $85.3 \pm 3.5 \%$ (10Ω) with increasing current generation (Fig. 3D). The highest ammonium removal efficiency with 10Ω doubles that under an open circuit condition. A linear relationship between current generation and ammonium removal efficiency was observed (R^2 of 0.969, inset, Figure 3D).

3.4 Effects of Water Flux

Water flux is playing an important role in the OsMFC because it can exert effects on water extraction, current generation and ion transport (and thus ammonium removal). To examine the effect of water flux, we investigated the ammonium removal in the presence or absence of water

flux. To obtain the same (or similar) current generation (so that we can exclude the effect of current generation), two conditions were created: first, 2 g L⁻¹ NaCl catholyte and 10 Ω external resistor; and second, 35 g L⁻¹ NaCl catholyte and 88 Ω resistor. The current densities of those two conditions were very similar at 0.9 ± 0.1 A m⁻² (Fig. 4A). However, they exhibited very different water flux, 0 ± 0.1 LMH in the first condition and 1.3 ± 0.2 LMH in the second condition, resulting in different ammonium removal efficiency of 47.8 ± 2.2 % and 74.2 ± 4.3 %, respectively (Fig. 4B). This demonstrates that water flux could promote ammonium transport from the anolyte into the catholyte. Some evidence might also be obtained from the prior results under the open circuit condition: the OsMFC with water flux (with 35 g L⁻¹ NaCl as the catholyte) achieved 40.7 ± 2.4 % of ammonium removal, much higher than 21.4 ± 2.2 % without water flux (with 2 g L⁻¹ NaCl as the catholyte) (Fig. 3B). A previous study has reported that the cation flux could be increased when sodium was in the feed solution and ammonium was in the draw solution in FO process, resulting from the ion exchange of cation ions (Lu et al., 2014a). But bioelectricity generation in an OsMFC could greatly inhibit back flux of cations (e.g., sodium ions) from the draw into the feed (Qin et al., 2016a) and facilitate forward movement of ammonium from the feed into the draw. Our analysis showed that ion exchange was not a major contributor to ammonium movement in the present OsMFC (more details in next section).

3.5 Mechanisms of Ammonium Movement

Despite the important role of current generation and water flux in ammonium removal, there also other mechanisms contributing to ammonium transport in the present OsMFC, such as ion diffusion and ion exchange. Thus, in total we identified four mechanisms of ammonium transport: (1) diffusion of ammonium ions due to a concentration gradient; (2) ammonium ion movement

from the anode to the cathode promoted by water flux; (3) ion exchange between anode ammonium ion and cathode sodium ions; and (4) migration of ammonium ions driven by current generation for charge balance. Those contributions were analyzed for improving our understanding (Fig. 5), but it should be noted that precise quantification is very difficult at this time because of simultaneous function of multiple mechanisms.

When the OsMFC was operated with 2 g L^{-1} NaCl catholyte in an open-circuit mode, there was neither current generation nor water flux and therefore, the ammonium removal was mainly attributed to the diffusion of ammonium ions and the ion exchange between sodium and ammonium (Fig. 5A). Based on the data of reverse fluxed sodium ions, the contribution of ion exchange was estimated to be only $0.4 \pm 0.1 \%$. Thus, the dominant transport mechanism in the absence of both water flux and electricity generation would be diffusion, which caused $21.0 \pm 2.2 \%$ of ammonium removal from the anode. We assumed the same diffusion contribution in other conditions due to the same ammonium gradient across the FO membrane, although some variation would be expected and warrant further investigation. A higher catholyte salinity of 35 g L^{-1} in the open circuit mode stimulated water flux, which contributed to $17.3 \pm 2.4 \%$ of ammonium transport, and improved the ion exchange contribution to $\sim 3\%$.

Current generation exhibited a significant contribution of $47.0 \pm 3.2 \%$ (35 g L^{-1}) and $26.4 \pm 2.2 \%$ (2 g L^{-1}). Increasing current density from 1.0 ± 0.1 to $1.8 \pm 0.1 \text{ A m}^{-2}$ also enhanced its contribution from $19.8 \pm 3.9 \%$ to $47.0 \pm 3.2 \%$ (Fig. 5B). It was observed that current generation decreased the contribution of ion exchange from $3.9 \pm 0.1 \%$ (open circuit mode) to $2.3 \pm 0.1 \%$ ($1.8 \pm 0.1 \text{ A m}^{-2}$). The contribution of water flux to ammonium removal was distinguished in the

condition of similar current generation (Fig. 5C). The contribution of current generation for both operations was similar at ~26 %. The condition of 35 g L⁻¹ NaCl catholyte and 88-Ω external resistance had additional 26.4 ± 4.4 % of ammonium removal, including 23.4 ± 4.4 % from water flux and 3.0 ± 0.2 % due to ion exchange. It was reported that proton flux could be enhanced in an OsMFC, compared to that of an MFC with cation exchange membrane (Zhu et al., 2015); ammonium ions have been considered as a proton shuttle (Cord-Ruwisch et al., 2011) and thus, water flux may also promote the transport of ammonium ions.

3.6 Implications and Perspectives

The present study, for the first time, demonstrated the feasibility of ammonium removal in an OsMFC that could be extended to nitrogen recovery from wastewater (Kelly and He, 2014). This new benefit - nitrogen removal/recovery of the OsMFC, in addition to energy production and water recovery, will create more application niches and improve technological sustainability. For example, wastewater containing a large amount of ammonium, such as digester effluent, animal wastewater, urine, and landfill leachate, can be treated in the OsMFC for contaminant removal and resource recovery. To further develop OsMFCs towards practical applications, several challenges must be properly addressed. First, the exact mechanism of water flux promoted ammonium transport should be better understood. This is important to integrate nitrogen recovery with water recovery in an FO-based system. Second, although we did not perform ammonia recovery in the present study, our prior work has shown that recovery (via ammonia stripping) would not be 100% efficient and there will be remaining ammonium in the catholyte (as high as 100-200 mg L⁻¹) (Qin and He, 2014). This ammonium residue can affect the quality of the produced water, and must be removed, for instance, during draw solute

regeneration. Third, it is not clear how ammonium transport/removal will be affected by the type of draw solute in an OsMFC. Especially, when a nitrogen-based draw solute such as ammonium bicarbonate (McCutcheon et al., 2006) or fertilizer (Phuntsho et al., 2011) is used for the purpose of easy regeneration, a smaller concentration gradient across the FO membrane could decrease ammonium transport from the anode into the cathode and thus lower the removal. In addition, RSF of nitrogen-based draw solute may also reduce ammonium removal efficiency. Last, system scaling up of the OsMFC and examination with actual wastewater for a long-term performance (for investigating system stability and membrane fouling) will be necessary and important.

4. CONCLUSIONS

Ammonium removal has been successfully achieved in an OsMFC. A higher anolyte flow rate would improve the transport of ammonium ions because of more organic inputs and thus higher current generation. The study confirmed that current generation was also a key factor to drive ammonium movement across FO membrane. The unique feature of the OsMFC (compared to conventional MFCs) - water flux was found to be able to promote ammonium transport from the anolyte into the catholyte. In addition to current generation and water flux, ion diffusion and ion exchange also contributed to ammonium movement. The findings of this study will help develop OsMFCs as a sustainable technology for resource recovery from wastewater.

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Figure Captions

Figure 1. Ammonium removal by the OsMFC affected by different catholyte NaCl concentrations: (A) current generation; and (B) water flux and NH_4^+ -N removal efficiency.

Figure 2. Ammonium removal by the OsMFC affected by different anolyte flow rates: (A) current generation and NH_4^+ -N removal efficiency; and (B) water flux.

Figure 3. Ammonium removal by the OsMFC affected by the current generation: (A) current generation in open and closed circuit conditions; (B) NH_4^+ -N removal efficiency in closed and open circuit conditions; (C) polarization curve; and (D) current generation and NH_4^+ -N removal efficiency with different external resistances.

Figure 4. Ammonium removal by the OsMFC affected by water flux: (A) similar current generation under two different conditions, 2 g L⁻¹ NaCl as catholyte / 10 Ω external resistance and 35 g L⁻¹ NaCl as catholyte / 88 Ω external resistance; and (B) NH_4^+ -N removal efficiency and water flux under those two conditions.

Figure 5. The contribution of different mechanisms to ammonium removal: (A) comparison between open and closed circuit conditions with or without water flux; (B) effects of current generation; and (C) effects of water flux (orange: current generation; green: water flux; yellow: ion exchange; and maroon: diffusion).

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