

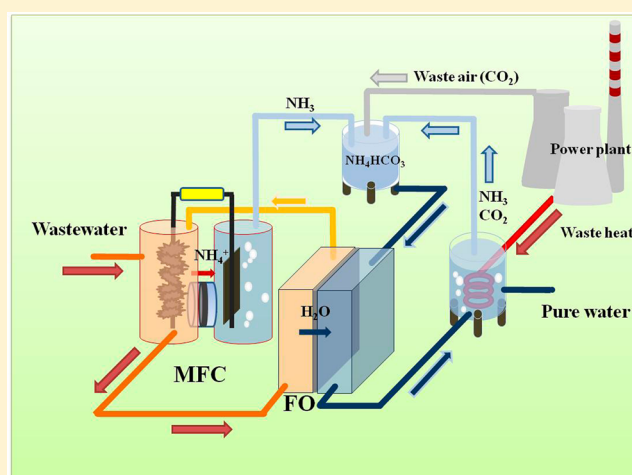
Self-Supplied Ammonium Bicarbonate Draw Solute for Achieving Wastewater Treatment and Recovery in a Microbial Electrolysis Cell-Forward Osmosis-Coupled System

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S Supporting Information

ABSTRACT: This study has presented a proof-of-concept system for the self-sustained supply of ammonium-based draw solute for wastewater treatment through coupling a microbial electrolysis cell (MEC) and forward osmosis (FO). The MEC produced an ammonium bicarbonate draw solute via recovering ammonia from a synthetic organic solution, which was then applied in the FO for extracting water from the MEC anode effluent. The recovered ammonium could reach a concentration of 0.86 mol L^{-1} , and with this draw solution, the FO extracted $50.1 \pm 1.7\%$ of the MEC anode effluent. The lost ammonium during heat regeneration could be supplemented with additional recovered ammonium in the MEC. The MEC achieved continuing treatment of both organic and ammonium in the returned feed solution mixed with fresh anolyte, although at lower efficiency compared to that with completely fresh anolyte. These results encourage further investigation to optimize the coordination between MEC and FO with improved performance.



INTRODUCTION

Wastewater reuse is critical to sustainable wastewater treatment and requires effective technologies to extract high-quality water from wastewater.¹ Membrane-based processes have been studied and/or employed to produce high-quality water from wastewater.² Among them, the forward osmosis (FO) process is of particular interest because of its low energy consumption and reduced membrane fouling.³ In a FO process, water moves across a semipermeable membrane from high water potential to low water potential driven by an osmotic pressure gradient.⁴

Draw solute plays a key role in creating an osmotic gradient for water extraction in FO.³ Because permeated water can dilute draw solution and some draw solutes may be lost due to reverse salt flux, draw solute needs to be recovered by additional processes or supplemented with fresh draw solute, thereby increasing the energy requirement and operating cost of the FO.⁵ Various types of draw solutes have been proposed,⁶ and among them, thermolytic ammonium salts, such as ammonium bicarbonate, have been demonstrated as an efficient and recyclable draw solute because of their high solubility, osmotic efficiency, and circulation capacity.⁷ More importantly, ammonium bicarbonate can be recovered using moderate heat, which has significant energy advantages compared with regeneration of other draw solutes.^{8,9} However, the application of ammonium bicarbonate as a draw solute has been limited

because of high reverse salt flux that causes the loss to the feed solution, which will not only require an additional supply of fresh draw solute but also deteriorate the quality of the remaining feed solution.¹⁰

The concentration of ammonium in some wastewaters such as digester centrate and landfill leachate can be over 500 mg L^{-1} .¹¹ Thus, recovering ammonia from wastewater may provide a sustainable approach for supplying draw solute to FO treatment, which is then used to treat the same wastewater. An innovative method for ammonium recovery from wastewater is using bioelectrochemical systems (BES).¹² During electricity generation, ammonium migrates from the anode (wastewater) into the cathode through a cation exchange membrane. It was found that high current generation could promote ammonium movement, and high pH of the catholyte facilitates the conversion of ammonium into ammonia gas, which can be stripped out of the catholyte and then recovered. To make a draw solute, carbon dioxide is needed. The anode reaction releases carbon dioxide; additional carbon dioxide may be supplied by combustion processes, for example, a power plant

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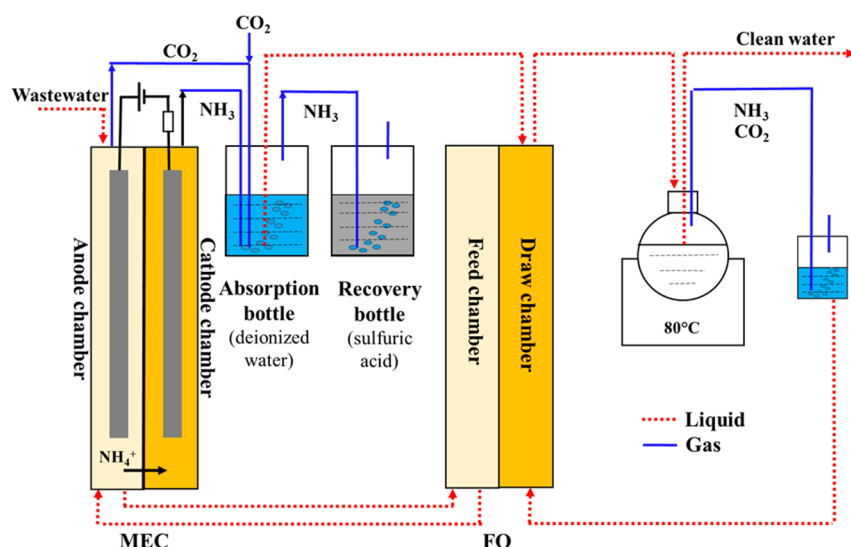


Figure 1. Schematic design of the MEC-FO-coupled system.

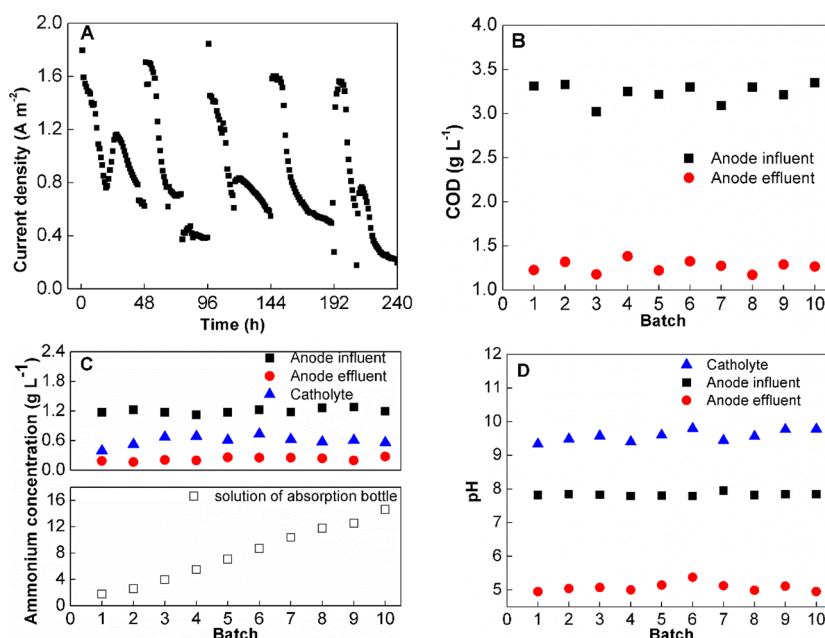


Figure 2. Ammonia recovery in the MEC: (A) current density, (B) COD concentration, (C) ammonium concentration in the MEC and solution of the absorption bottle, and (D) pH in each chamber.

that provides both carbon dioxide and low heat for recovering ammonium bicarbonate.¹³

Herein, we investigated the feasibility of the above concept with a coupled system consisting of a microbial electrolysis cell (MEC) and an FO; the MEC was to degrade organic compounds (in its anode) and recover ammonia (in the cathode) for preparing draw solute for the following FO treatment that extracted clean water from the MEC anode effluent. The key parameters, including ammonia recovery and regeneration, organic degradation, electricity generation, and water flux, were investigated.

MATERIALS AND METHODS

The MEC-FO System. A bench-scale MEC-FO system consisted of two units, a MEC unit and a FO unit, which were linked through two liquid streams (Figure 1). The synthetic organic solution was fed into the anode chamber of the MEC,

and its effluent then flowed into the feed side of the FO. The gas streams from the anode and cathode of the MEC were channeled through two 100 mL glass bottles. The first bottle was an absorption bottle filled with deionized water to collect gaseous ammonia (NH₃) and CO₂ to generate ammonium bicarbonate. Additional carbon dioxide was introduced into this bottle at a flow rate of 1.26 mL min⁻¹ by a CO₂ cylinder. The second bottle was filled with 1 M sulfuric acid (H₂SO₄) to absorb the excessive NH₃ that could not be captured by the first bottle, named “recovery bottle”. Once the concentration of ammonium ions in the absorption bottle reached 0.80 M, the solution was transferred to the FO as the draw solution for water extraction from the treated organic solution (from the MEC anode). When the water flux in the FO dropped below 1.0 L m⁻² h⁻¹ (LMH), the diluted draw solution was sent to a heat recovery unit, in which the temperature was set at 80 °C. The NH₃ and CO₂ were separated from the draw solution and

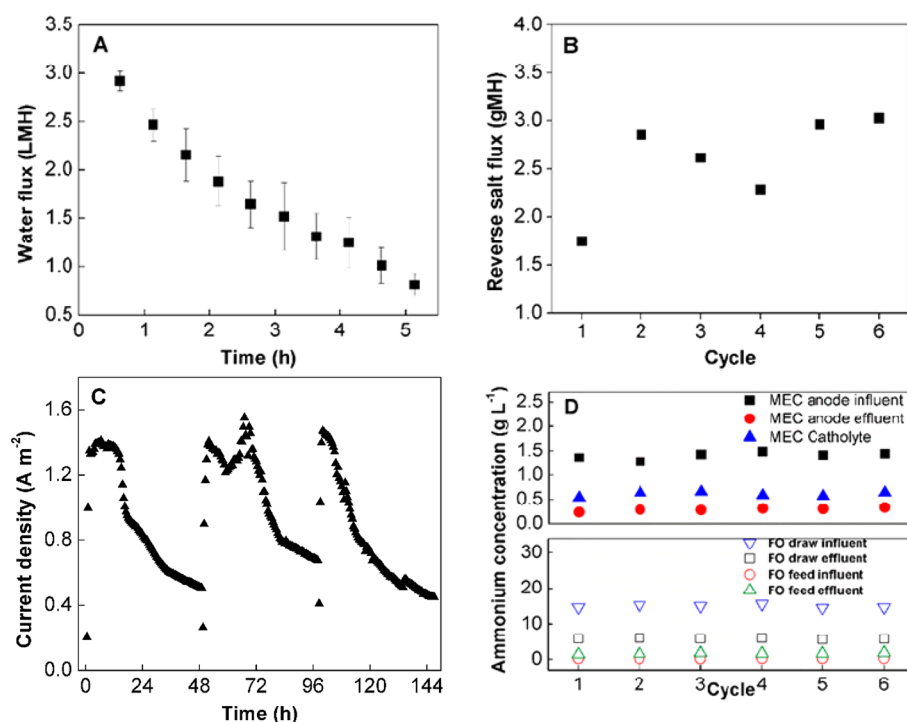


Figure 3. MEC–FO system: (A) water flux in the FO process, (B) reverse salt flux in FO, (C) current density from the mixture of returned feed solution and fresh anolyte in the MEC, and (D) ammonium concentration in the MEC and FO.

flowed into an adsorption flask containing deionized water to regenerate the draw solution. The concentrated feed solution from the FO was adjusted to pH 7.0 with 80 μL of 0.1 M NaOH solution and returned to the MEC for further treatment.

MEC and FO Setup and Operation. A tubular MEC was constructed (details in the Supporting Information). A 1 m long carbon brush was folded to fit into the anode compartment as the anode electrode. The cathode electrode was a piece of carbon cloth (160 cm^2) coated with platinum/carbon as a catalyst (0.3 mg Pt cm^{-2}).¹⁴ The cathode compartment was aerated to provide oxygen for reaction and to strip ammonia from the catholyte.¹⁵ The synthetic organic solution that mimicked piggery wastewater or its anaerobic digestion effluent^{16,17} contained the following (per liter of deionized water): glucose, 3.0 g; NH_4Cl , 3.0 g; NaHCO_3 , 5.0 g; NaCl, 0.5 g; MgSO_4 , 0.015 g; CaCl_2 , 0.02 g; and trace elements, 1 mL.¹⁸ An external voltage of 0.8 V was applied to the circuit by a power supply (CSI3644A, Circuit Specialists, Inc., Mesa, AZ, U.S.A.) according to a previous study.¹⁹

A SEPA CF Cell (Sterlitech Corporation, Kent, WA, U.S.A.) was used as a FO cell. The FO membrane was cellulose triacetate (Hydration Technologies, Inc., Albany, OR, U.S.A.) and was installed with its active layer facing the feed solution. During the operation, both the feed solution and draw solution were recirculated at 96 mL min^{-1} . The water flux (LMH) is calculated by the change in weight of the feed or draw solution.²⁰ The reverse salt flux ($\text{g m}^{-2} \text{h}^{-1}$, gMH) from the draw side to the feed side was calculated by measuring the salt concentration change in the feed solution.²⁰ More details about measurement and analyses can be found in the Supporting Information.

RESULTS AND DISCUSSION

Preparing the draw solution and generating the feed solution were examined in the MEC via investigating the ammonia

recovery and treatment of the synthetic organic solution. Under an applied voltage of 0.8 V, the MEC produced $1.8 \pm 0.1 \text{ A m}^{-2}$ (Figure 2A) and decreased the COD concentration from 3.23 ± 0.16 to $1.27 \pm 0.08 \text{ g L}^{-1}$, representing a COD removal efficiency of $60.6 \pm 2.2\%$ ($0.98 \pm 0.07 \text{ kg m}^{-3} \text{ d}^{-1}$) (Figure 2B).

The ammonium concentration in the anolyte decreased from 1.19 ± 0.11 to $0.22 \pm 0.06 \text{ g L}^{-1}$, representing removal of $81.5 \pm 4.4\%$ ($0.49 \pm 0.04 \text{ kg m}^{-3} \text{ d}^{-1}$) (Figure 2C). The catholyte had an ammonium concentration of $0.60 \pm 0.15 \text{ g L}^{-1}$. Assuming one electron moves one ammonium ion from the anode chamber into the cathode chamber, migration of ammonium ions could contribute to 48.9% of ionic flux through the CEM, indicating that ammonium ions acted as a proton shuttle in the MEC system.²¹ The catholyte pH increased from 6.89 to 9.33 (Figure 2D). The aeration in the cathode compartment promoted the stripping of ammonia out of the catholyte.²² Although the catholyte pH of the present MEC was lower than that of a MEC without aeration (up to 13²³), the lower catholyte pH could decrease the cell overpotential and improve system stability.²⁴ The stripped ammonia was collected in the absorption bottle, in which the ammonium concentration increased gradually to 14.6 g L^{-1} ; 45.3% of input ammonium was recovered by deionized water in the absorption bottle, while 26.1% was collected by sulfuric acid in the recovery bottle. The gas analysis shows that $87.3 \pm 3.4\%$ of gas generated from the anode was CO_2 . The volume of generated CO_2 in one batch was about 47 mL, which was not enough for generating ammonium bicarbonate (considering the ratio between ammonium and carbon dioxide). Thus, additional CO_2 was added into the adsorption bottle. After 10 batches, the ammonium concentration reached 14.6 g L^{-1} (Figure 2C), representing 0.86 mol L^{-1} ammonium bicarbonate.

The generated ammonium bicarbonate solution was transferred to the FO as a draw solution for water recovery from the

MEC anode effluent. The results demonstrated the effectiveness of this draw solution. The FO achieved a maximum water flux of 2.9 ± 0.1 LMH, within the range of the FO processes using ammonium bicarbonate as a draw solution in other studies.^{7,25} The water flux decreased to 0.8 ± 0.1 LMH after a 5 h operation (Figure 3A), and $50.1 \pm 1.7\%$ of the MEC anode effluent was extracted into the draw side. After the FO treatment, the ammonium concentration in the feed solution increased from 0.24 ± 0.03 to 1.66 ± 0.15 g L⁻¹, likely because of the concentrating effect due to reduced liquid volume and ammonium intrusion from the draw side via reverse salt flux. It was determined that the reverse salt flux was 2.6 ± 0.4 gMH (Figure 3B), with a salt rejection of $87.9 \pm 1.8\%$. During regeneration of the draw solution in the heat recovery unit, 83.1% of ammonium was recovered at 80 °C, and the lost part was supplied by the additionally recovered ammonia in the MEC. A lower recovery temperature at 60 °C achieved only 51.1% of ammonium recovery. After heat regeneration, the extracted water contained less than 1 mg L⁻¹ of ammonium and undetected COD.

The concentrated feed solution from the FO was mixed with fresh anolyte (~1:1), and then the mixture was fed into the MEC anode compartment in the following cycle. The COD concentration in the mixture was 3.07 ± 0.28 g L⁻¹, and the concentration of ammonium was 1.40 ± 0.08 g L⁻¹. The MEC fed with the mixed influent generated 1.5 ± 0.1 A m⁻² (Figure 3C), lower than that with the fresh feeding solution (1.8 ± 0.1 A m⁻²) possibly because of lower COD input and accumulation of soluble microbial products (SMP).^{26,27} The lower current resulted in a relatively lower COD removal efficiency of $47.1 \pm 3.5\%$ (0.73 ± 0.12 kg m⁻³ d⁻¹) but had minor influence on ammonium recovery ($79.7 \pm 2.0\%$, 0.56 ± 0.04 kg m⁻³ d⁻¹). After six cycles, the conductivity of the MEC anolyte slightly increased from 6.09 to 7.65 mS cm⁻¹ because of the concentrated salts during the FO process. Increased conductivity in the anolyte could decrease the water flux in the FO due to a decreased salt gradient. It is expected that salts will build up over time to a level that will significantly affect water flux. At that time (which needs to be further verified), the anolyte may be disposed, and the MEC will receive 100% fresh organic solution to start a new cycle.

We have analyzed the mass distribution for both carbon and ammonium (details in the Supporting Information) and found that the system would need multiple batches to resupply the lost ammonium and carbon dioxide due to reverse salt flux and during regeneration. Improving regeneration efficiency will make it possible to resupply ammonium via a one-batch operation, but CO₂ is still insufficient because of low anolyte pH that retains most CO₂ as carbonate acid. An external supply of CO₂ will be necessary, and there is a readily available source during wastewater treatment, e.g., combustion of methane gas produced in an anaerobic digester that can also provide heat for regeneration of draw solute. Because of the need for supplementing the lost draw solutes, low-strength wastewater may not be a suitable target for the present system because of its low concentrations of both organics and ammonium. The organic solution used here mimicked some types of animal wastewater, and the wastewaters such as digestion effluent of other wastes and leachate containing higher concentrations of organics and/or ammonium will also be of interest for this system.

In the MEC, the energy input was 3.9 kWh m⁻³ of treated water (2.0 kWh kg⁻¹ COD, or 5.1 kWh kg⁻¹ N, more

information is in the Supporting Information), among which 53.8% was consumed by the external power supply, 16.8% was due to the aeration in the cathode, and 29.4% was consumed by the anolyte recirculation. In the FO, the energy input was 0.1 kWh m⁻³. To eliminate the major energy requirement by the external power supply, microbial fuel cells (MFCs) may replace MECs for ammonia recovery. We will investigate the use of MFCs and evaluate the relationship between reduced energy consumption and decreased treatment efficiency.

These results have successfully demonstrated the feasibility of coupling an ammonia-recovering MEC with FO for treating organic solutions and recovering valuable resources (e.g., ammonia and water). Such cooperation provides a sustainable source of ammonium-based draw solute for FO. Establishing a loop operation of wastewater between the MEC anode and the FO feed side could alleviate the effect of reverse ammonium flux on the effluent quality with further treatment/recovery in the MEC. The hydraulic retention time in each unit of the system needs to be better coordinated because of uneven treatment speed between the two. Nevertheless, this proof-of-concept system encourages further studies of system optimization with examination of actual wastewaters.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Analysis of mass balance and energy. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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