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Capacitive Membrane Stripping for Ammonia Recovery (CapAmm) from Dilute Wastewaters

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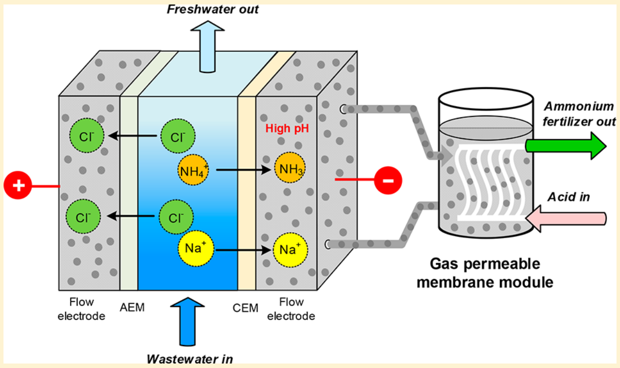
Supporting Information



ABSTRACT: A novel cost-effective flow-electrode capacitive deionization unit combined with a hydrophobic gas-permeable hollow fiber membrane contactor (designated "CapAmm") is described here and used for efficient recovery of ammonia from dilute synthetic wastewaters. During operation, ammonia migrates across a cation exchange membrane and selectively accumulates in the cathode chamber of a flow electrode followed by transformation to dissolved NH_3 with subsequent stripping via a membrane contactor and recovery as ammonium sulfate. Our results demonstrate that the CapAmm process can achieve an ammonia removal efficiency of ∼90% and a recovery efficiency of ∼60%. At current densities of 5.8 and 11.5 A m^{-2} (normalized by the effective cation exchange membrane area) and a hydraulic retention time of 1.48 min, the energies required for ammonia recovery were 9.9 and 21.1 kWh (kg of N)$^{-1}$, respectively, with these values being comparable with those of other similar electrochemical ammonia recovery systems. These findings suggest that the CapAmm technology described here has the potential for the dual purposes of cost-effective salt removal and the recovery of ammonia from wastewaters, with greater stability, better flexibility, and greater energy efficiency compared to those of other methods.

INTRODUCTION

A rapidly increasing world population and improvement in living standards have resulted in greater demand for food production, with this production being strongly dependent on the utilization of fertilizers rich in nitrogen (N) and phosphorus (P) to maintain soil fertility and increase crop yields.[1,2] However, the traditional Haber-Bosch process for the production of ammonia, the key component in the synthesis of most popular N fertilizers (including urea, ammonium nitrate, and ammonium sulfate), is responsible for 1.5−2.5% of the annual global energy consumption and more than 1.6% of global CO_2 emissions.[3−5] Considering that the demand for nitrogen fertilizer is expected to increase at an average annual growth rate of 1.5% over the next decade,[6,7] the issue of how to produce ammonia in a sustainable manner represents a global challenge.

While the amount of money spent on ammonia production for fertilizer use is increasing, water contamination has become increasingly severe, especially in recently industrialized countries such as China and India, with ammonia nitrogen recognized to be one of the principal contaminants. It has been reported that 2.5 million t of ammonia nitrogen is discharged annually to water bodies in China,[2] with the injection of this major nutrient resulting in severe eutrophication, acute and chronic toxicity to aquatic organisms, and production of toxic byproducts during drinking water disinfection.[8,9] Though a great number of robust technologies such as nitrification/denitrification, electrochemical oxidation, and breakpoint chlorination have been developed to remove ammonia from wastewaters,[10−14] this practice would seem to be unsustainable in view of the life cycle of ammonia mentioned above. In light of the problems associated with removal of ammonia from waters and the increasing demand for ammonia-based fertilizers, there is growing interest in the recovery of ammonia from dilute wastewaters in view of the economic and environmental benefits.[15−17]

The first step in the recovery of ammonia from low-strength wastewaters involves preconcentration of the ammonia. While ion exchange adsorption by zeolites and membrane separation (e.g., reverse osmosis and nanofiltration) may be used to generate ammonia-rich solutions,[18,19] these technologies suffer from a high energy cost and/or require large quantities of chemicals for regeneration purposes and, as a result, are less

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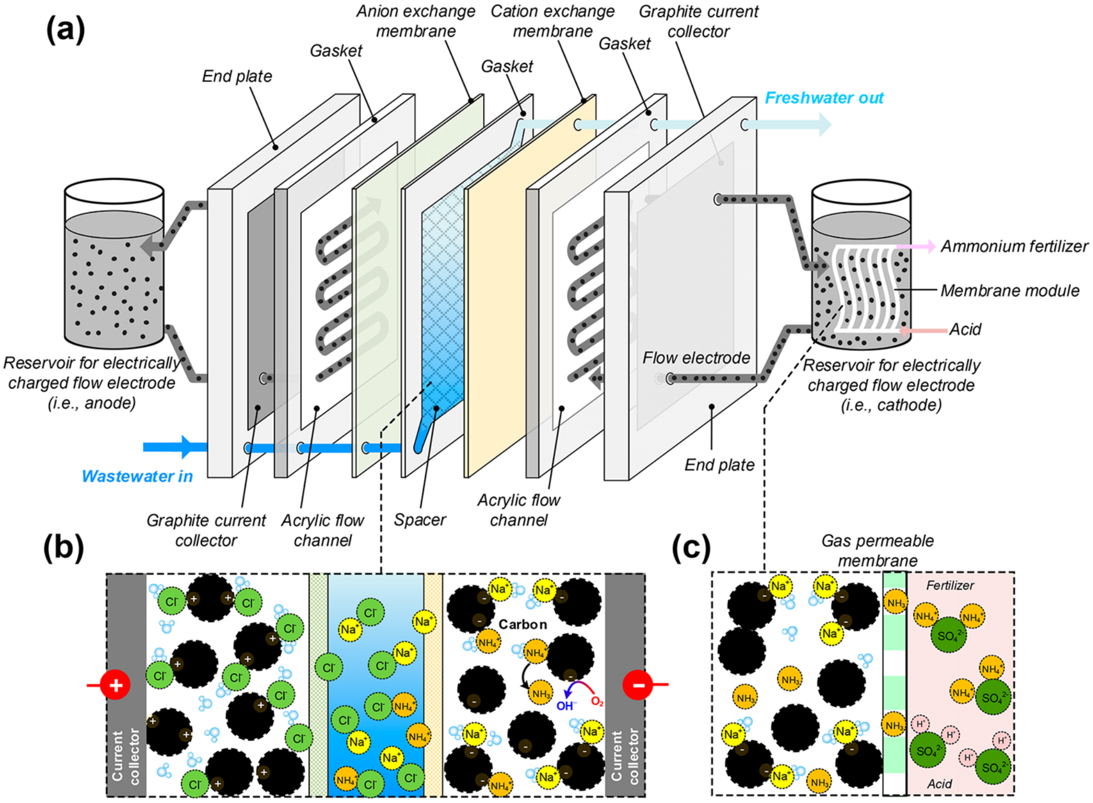
Scheme 1. (a) Capacitive Membrane Stripping for Ammonia Recovery (CapAmm), (b) Ammonia Migration and Transformation in the Desalination Unit, and (c) Selective Recovery of Ammonia from the Negatively Charged Flow Electrode



feasible for the recovery of ammonia from dilute waste streams. Recently, flow-electrode capacitive deionization (FCDI) has attracted interest given its potential applications in seawater desalination and energy storage.[19−22] FCDI is particularly effective for the accumulation of ions in the flow electrodes, with cations such as Na^+ and NH_4^+ concentrated in the cathode chamber and anions such as Cl^- concentrated in the anode chamber. In addition to this capacitive mechanism, electron exchange at the surface of the flow electrodes may well result in the consumption and/or production of protons.[23] An increase in the pH in the cathode chamber (as is typical as a result, in part, of the reduction of oxygen)[23,24] would result in a change in speciation from NH_4^+ dominance at pH < pK_a (of 9.3) for the NH_4^+−NH_3 acid−base pair to $NH_3(aq)$ dominance at pH > pK_a. Equilibrium will rapidly be established between dissolved and gaseous ammonia in the cathode chamber, with the possibility of subsequent removal of $NH_3(g)$ by interfacing the solution with a gas-permeable membrane.

In this study, we develop a process for capacitive membrane stripping for recovery of ammonia (CapAmm) from dilute wastewaters (Scheme 1), in which ammonia migrates across a cation exchange membrane and selectively accumulates in the cathode chamber of a flow electrode followed by transformation to dissolved NH_3 with subsequent stripping via a membrane contactor and recovery in an acidic solution [for example, as $(NH_4)_2SO_4$]. A number of operational parameters associated with the performance of CapAmm are investigated with specific consideration given to the mass flow of ammonia from the influent wastewater to the acidic receiving solution. An overall evaluation of the operating cost and economic benefit of the ammonia produced highlights the opportunities and challenges of CapAmm with respect to sustainable water, resource, and energy management.

■ MATERIALS AND METHODS

Experimental Setup. The structure of the CapAmm apparatus is shown in Scheme 1a and Figure S1. A silicone gasket and a nylon sheet (100 mesh) were bounded by two ion exchange membranes (CEM-Type I/AEM-Type I, FUJIFILM Europe) with the gap between the ion exchange membranes acting as a spacer chamber (thickness of ~500 μm) through which the wastewater flowed (Scheme 1b).[21,25] Acrylic sheets with carved serpentine channels for flow electrodes were placed against the graphite current collectors (Scheme 1a). The cross section of each channel was 3 mm × 3 mm with an effective contact area between the ion exchange membrane and the flow electrodes of 34.9 cm^2. These parts were held together with the use of acrylic end plates (Scheme 1a and Figure S2). The flow electrodes were continuously cycled between the flow channels and the circulation tanks, with the polypropylene (PP) hollow fiber membrane contactor (Scheme 1a,c) placed in the negatively charged flow-electrode circulation tank. The total length of the membranes used in this work was 30 cm, with an outer diameter of 2 mm, a wall thickness of 0.1 mm, a pore size of 0.45 μm, and a total effective surface area of 18.8 cm^2.

Operating Conditions. Synthetic wastewater containing 1000 mg L^{-1} NaCl and 40 mg L^{-1} NH_4^+-N was fed into the spacer chamber in single-pass mode. The effect of different wastewater flow rates [from 0.85 to 2.55 mL min^{-1} with corresponding hydraulic retention times (HRTs) from 2.94 to 0.98 min, respectively] was evaluated in this study. The electrical conductivity of this stream was continuously

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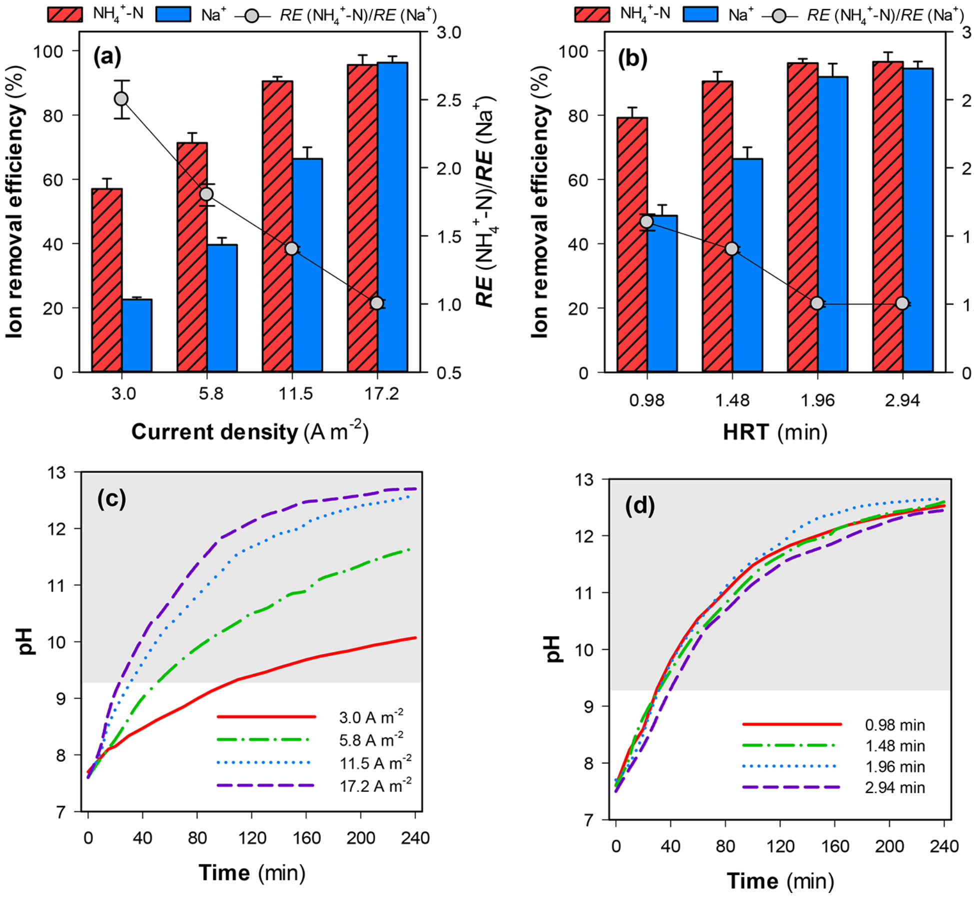


Figure 1. Average removal efficiencies for ammonium and sodium ions in the CapAmm system (a) at different current densities (i.e., 3.0, 5.8, 11.5, and 17.2 A m^{-2}) with a constant HRT of 1.48 min and (b) at a constant current of 11.5 A m^{-2} with HRTs of 0.98, 1.48, 1.96, and 2.94 min. The blue symbols are the ratios of removal efficiency [RE(NH_4^+-N)/RE(Na^+)], with this ratio representing the selectivity of NH_4^+ compared to Na^+. Temporal change of pH in the cathode chamber of the CapAmm system operated (c) under different current densities (i.e., 3.0, 5.8, 11.5, and 17.2 A m^{-2}) with a constant HRT of 1.48 min and (d) under a constant current of 11.5 A m^{-2} with different HRTs (i.e., 0.98, 1.48, 1.96, and 2.94 min). The shaded area represents the pH range of >9.3, indicating the deprotonation of NH_4^+ to NH_3.

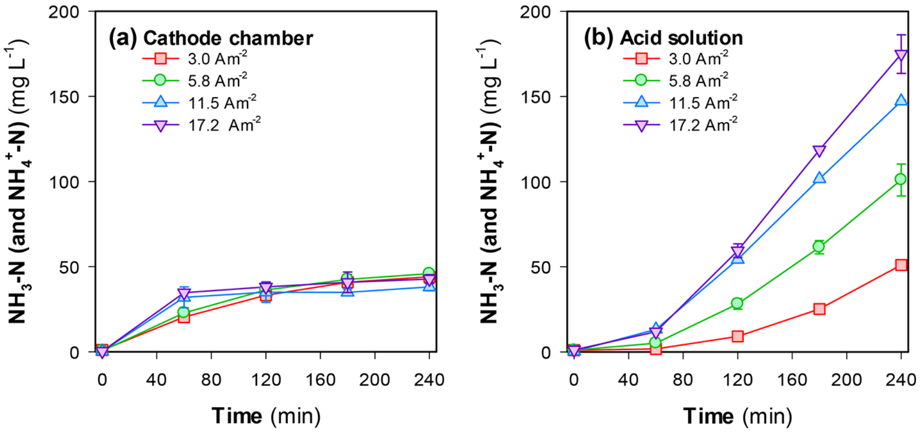
measured at the outlet with the use of a conductivity meter (CON-BTA, Vernier) connected to a data acquisition system (SensorDAQ, Vernier). The flow electrodes were composed of 10 wt % 100 mesh DARCO-activated carbon (which, on the basis of scanning electron microscopy images, exhibited an average particle size on the order of 18.5 μm) and 90 wt % Milli-Q water and were prepared in a manner identical to that described in our earlier studies.[21] In all experiments, the 65 mL flow electrodes were recirculated using a dual-head peristaltic pump (Longer pump, Baoding, China) at a constant flow rate of 50 mL min^{-1}. In one operating cycle, electrosorption was performed at a constant current density (3.0−17.2 A m^{-2}) using a dc power supply (MP3840, Powertech). For ammonia recovery, the membrane module was immersed in the cathode flow-electrode slurry while 65 mL of receiving solution (0.5 M sulfuric acid) was continuously circulated (at 50 mL min^{-1}) inside the hollow fiber membranes.[26,27] The ammonia dissolved in the flow-electrode slurry evaporates and diffuses through the pores of the gas-permeable membrane and then reacts with sulfuric acid, resulting in the formation of ammonium sulfate (the detailed mechanism is shown in SI text 1 and Figure S3). The analytical methods and calculations are presented in the Supporting Information.

RESULTS AND DISCUSSION

Removal of Ammonia from the Dilute Wastewater.

Results for salt removal performance in the CapAmm system at different charging current densities and HRTs are summarized in Figure S4 and Figure 1. Relatively stable effluent conductivity was observed under all experimental conditions, with higher current densities and longer HRTs resulting in a greater reduction in feedwater conductivity (Figure S4). Meanwhile, increases in both applied current densities and HRTs also exert positive effects on NH_4^+ and Na^+ removal. It is also revealed that CapAmm has a higher selectivity for NH_4^+-N than for Na^+ removal, particularly at a lower current density and/or HRT (Figure 1a,b). For instance, the ratio of removal efficiency between NH_4^+-N and Na^+ [i.e., RE(NH_4^+-N)/RE(Na^+)] was 2.5 at a current density of 3.0 A m^{-2} but gradually decreased to 1.8, 1.34, and 1.0 at higher current densities of 5.8, 11.5, and 17.2 A m^{-2}, respectively. A similar trend was observed for the effect of the change in HRT with RE(NH_4^+-N)/RE(Na^+) declining from 1.6 to 1.0 with an increase in HRT from 0.98 to 2.94 min. The change in current efficiency is described in the Supporting Information (see Figure S5).

It has previously been reported that ions with a smaller hydrated radius are transported more rapidly from the feedwater into the cathodic flow electrode under a fixed



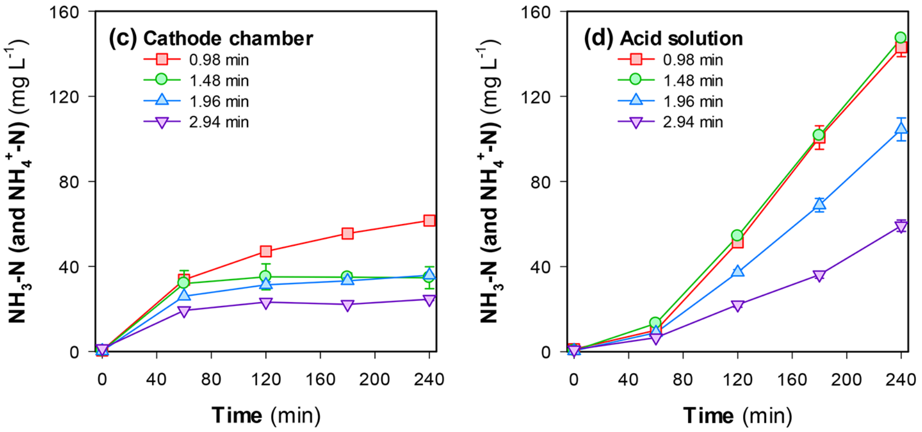


Figure 2. Temporal variation of the ammonia concentration in (a) the cathode chamber and (b) the acidic receiving solution of the CapAmm system operated under different current densities (i.e., 3.0, 5.8, 11.5, and 17.2 A m^{-2}) with a constant HRT of 1.96 min and the ammonia concentration in (c) the cathode chamber and (d) the acidic receiving solution of the system charged at a constant current density of 11.5 A m^{-2} with different HRTs (i.e., 0.98, 1.48, 1.96, and 2.94 min).

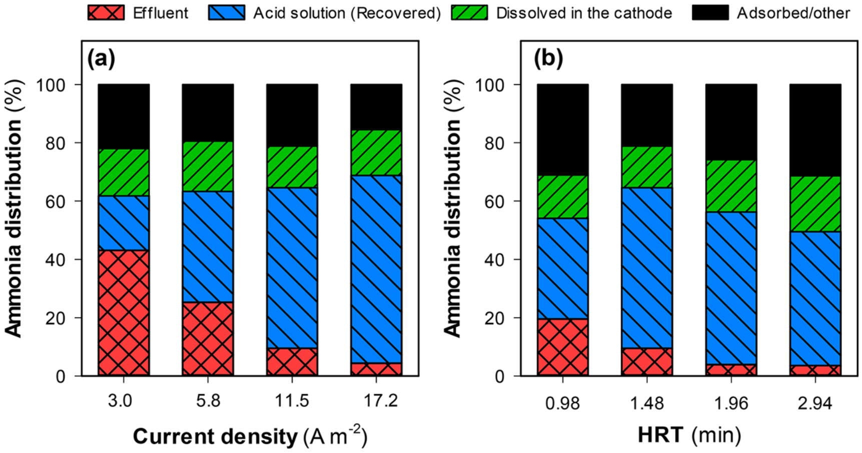


Figure 3. Fate and distribution of ammonia in the CapAmm system (a) at different current densities (i.e., 3.0, 5.8, 11.5, and 17.2 A m^{-2}) with a constant HRT of 1.96 min and (b) at a constant current of 11.5 A m^{-2} with different HRTs (i.e., 0.98, 1.48, 1.96, and 2.94 min).

electrical field, provided that they have the same valence charge.[28] Additionally, smaller ions are more readily electrosorbed by activated carbon particles than larger ions are because of their easier access to the micropores of these particle electrodes.[29,30] The fact that NH_4^+ has a hydrated radius (3.31 Å) that is slightly smaller than that of Na^+ (3.58 Å)[31] may account for the observation that the electrosorption process in our CapAmm system exhibits a higher selectivity toward NH_4^+ than toward Na^+ at lower current densities and shorter HRTs.

Transformation of Ammonia in the Flow Electrode. Panels c and d of Figure 1 indicate that the pH of the cathode gradually changed from neutral to alkaline during operation. The shaded areas represent the region in which the pH was higher than the pK_a of NH_4^+ (9.3). In this region, almost all of the NH_4^+ will be deprotonated and transformed into dissolved

NH_3(aq), thereby providing ideal prerequisites for ammonia separation and recovery from the bulk solution via membrane stripping.

According to recent studies, Faradaic reactions such as oxygen reduction take place at the cathode even when the cell voltage is relatively low (e.g., <1.0 V), consuming H^+ and resulting in an increase in pH.[23,32−34] It is to be expected that higher current densities (and higher charging voltages) will facilitate oxygen reduction, leading to a more rapid increase in the pH in the cathode. In contrast, changing HRTs does not influence the duration for which the flow electrode is exposed to a particular applied potential (as the flow electrode is recirculated at a constant rate) and, as such, would not be expected to significantly influence the pH.

Ammonia Recovery and Energy Consumption. As shown in Figure 2, one can conclude that ammonium ions removed from the feed stream were effectively transferred to the acidic receiving solution, with the recovered NH_4^+-N concentrations finally reaching 51.1 ± 1.2, 100.1 ± 9.6, 147.2 ± 0.6, and 174.9 ± 11.4 mg L^{-1} at 3.0, 5.8, 11.5, and 17.2 A m^{-2}, respectively (Figure 2a,b). The average ammonia recovery rate increased from 5.7 to 19.5 g of N m^{-2} day^{-1} when the current density increased from 3.0 to 17.2 A m^{-2}. In the first hour, the NH_4^+-N concentration in the acid solution increased relatively slowly, presumably because the initial low pH in the cathode chamber (Figure 1c,d) hindered the transformation of NH_4^+ into NH_3(aq) and the subsequent diffusion of NH_3(g) across the gas membrane. When the NH_4^+-N concentration in the cathode solution was analyzed, a sharp increase was observed in the first hour, and then the value reached a relatively stable concentration of 35−40 mg L^{-1} in the following 3 h (Figure 2a). Similar trends were observed upon operation under different HRTs (Figure 2c,d).

From Figure 3a, we can clearly see that the applied current density plays an important role in ammonia recovery. At current densities of >11.5 A m^{-2}, 55−65% ammonia can be recovered by the membrane contactor as ammonium fertilizer, ∼15% of the ammonia is still present in the cathode, and 20% is not detected (presumably either because it is electro-absorbed on the carbon particles or because it has been air-stripped). It would be particularly advantageous if the ammonia remaining in the cathode chamber (∼35% of the total) could be recovered. As Figure 3b makes clear, HRTs have a minor influence on the ammonia recovery efficiency, especially when the HRT is >1.48 min, with a similar recovery rate at these long HRTs of 50−60%.

An overview of the effluent water quality, NH_4^+-N recovery efficiency, energy consumption, and average ammonia removal/recovery rate over a range of operating conditions is provided in Table S1. Overall, the energy required for water desalination ranged from 0.05 to 1.95 kWh m^{-3}, depending on the applied current densities and HRTs.

At applied current densities of 3.0, 5.8, and 11.5 A m^{-2} (for an HRT fixed at 1.48 min), the energies consumed for ammonia recovery were 6.1, 9.9, and 21.7 kWh (kg of $N)^{-1}$ with recovery efficiencies (respectively) reaching 18.7, 38.1, and 55.1% and calculated average recovery rates of 5.7, 11.3, and 16.5 g of N m^{-2} day^{-1}, respectively. The energy consumption of the CapAmm system is comparable with those of other electrochemical ammonia recovery systems. For instance, an integrated system composed of a hydrogen gas (H_2) recycling electrochemical cell (recycling of the H_2 generated at the cathode to the anode) and a gas-permeable membrane contactor was found to achieve an ammonia recovery efficiency of 60−73% and an average ammonia recovery rate 110.2 g of N m^{-2} day^{-1} at an energy requirement of 10.0 kWh (kg of $N)^{-1}$.[35] However, this system required the injection of additional H_2 and the application of a noble catalyst to enable stable operation, with these components representing an additional energy cost.[35] Another ammonia recovery system that combined an electrochemical cell (EC) and air stripping was able to recover 96% ammonia at a recovery rate of 120 g of N m^{-2} day^{-1} and exhibited an energy consumption of 20 kWh (kg of $N)^{-1}$ [with 13 kWh (kg of $N)^{-1}$ for EC and 9 kWh (kg of $N)^{-1}$ for air stripping].[36] More importantly, it should be noted that most of these ammonia recovery systems were focused on harvesting ammonia from high-ammonia concentration (∼3400 mg L^{-1} N) streams (such as urine) with relatively low concentrations of competing ions (∼1400 mg L^{-1} K^+ and ∼1600 mg L^{-1} Na^+), with the competing cation to NH_4^+-N mole ratio being as low as 0.43. However, the influent of our CapAmm system contains 40−50 mg L^{-1} NH_4^+-N (∼80 times lower than that in urine) and ∼390 mg L^{-1} Na^+ (∼1000 mg L^{-1} NaCl), resulting in a high Na^+/NH_4^+-N mole ratio of 5.7. This means that a larger portion of the energy will be consumed for water desalination (salt removal), thereby resulting in a relatively lower ammonia recovery rate. In our future studies, we will examine the applicability (and energy usage) of the CapAmm process for the recovery of ammonia from medium- to high-ammonia concentration waste streams.

In contrast, bioelectrochemical systems (BES), which take advantage of electrochemically active bacteria to degrade organic matter and generate electricity, can recover ammonia at much a lower energy demand compared to traditional EC systems and the CapAmm system introduced here.[37−40] In BES, however, the ammonia recovery rate is relatively slow (3−5 g of N m^{-2} day^{-1})[17,37] because of the limited current density produced by the anaerobic bacteria at the anode. Additionally, the biological process is very sensitive to a range of environmental factors, including pH, carbon loading, chemical toxicity (e.g., ammonia present in the influent), and temperature, restricting the practical application of these technologies. Indeed, the CapAmm process may have an advantage over BES in view of its greater stability, predictability, and flexibility and the opportunity for automatic control of the reactor.

■ IMPLICATIONS

Our study demonstrates that the CapAmm process can be a very effective alternative for removal and recovery of ammonia from dilute wastewaters. Compared with other ammonia recovery systems that require additional chemical dosing to adjust the pH and use energy-intensive air stripping to extract ammonia, CapAmm allows for the selective removal of ammonia from the wastewater stream and preconcentration in the cathode chamber, with the increase in pH that occurs as a result of intrinsic Faradaic processes favoring the conversion of NH_4^+ to dissolved NH_3(aq). Given the rapidity with which solution phase ammonia equilibrates with gaseous ammonia, NH_3(g) will readily diffuse through a gas-permeable membrane into an acid solution and may be recovered as an ammonium salt that can, potentially, be readily marketed as a fertilizer. In addition, our experimental setup is less complex than other experimental configurations that utilize energy-intensive air-stripping processes or require the use of multiple absorption vessels. While sulfuric acid was used in this study for ammonia recovery, alternative acids (such as phosphoric acid or nitric acid) could be used to produce higher-value fertilizers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00534.

> Detailed information about the construction of the CapAmm cell, analytical methods and calculations, mechanism of recovery of ammonia by gas-permeable membranes, variation of effluent conductivity, variation of current efficiency, and comparison of effluent water quality, ammonia recovery efficiency, energy consumption, and ammonia removal/recovery rate over a range of operating conditions (PDF)

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Notes

The authors declare no competing financial interest.

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