

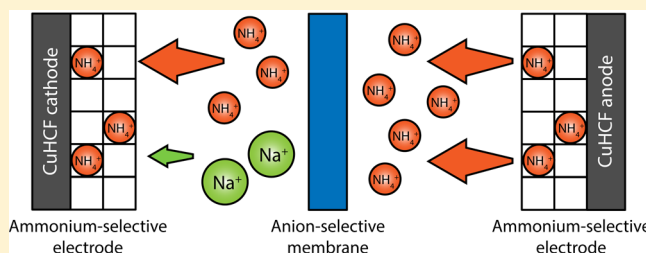
Ammonium Removal from Domestic Wastewater Using Selective Battery Electrodes

Taeyoung Kim,¹ Christopher A. Gorski,¹ and Bruce E. Logan^{1*}

Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

Supporting Information

ABSTRACT: Conventional technologies for ammonium removal from wastewaters are based on biological conversion to nitrogen gas, eliminating the possibility for ammonium recovery. A new electrochemical approach was developed here to selectively remove ammonium using two copper hexacyanoferrate (CuHCF) battery electrodes separated by an anion exchange membrane, at low applied voltages (0.1 to 0.3 V). The CuHCF battery electrodes removed NH_4^+ from a synthetic wastewater with a selectivity >5 (i.e., percent removed of NH_4^+ /percent removed of Na^+) when operated with a 0.1 V applied voltage, despite the much higher initial Na^+ concentration in the sample (20 mM) than NH_4^+ (5 mM). In contrast, we observed only negligible selective removal of NH_4^+ over Na^+ (<2) when using nonselective electrodes or ion-selective membranes (10 mM Na^+ , 5 mM NH_4^+ , 0.1 V). The selectivity further increased to 9 when using equimolar concentrations of NH_4^+ and Na^+ (10 mM). With an actual domestic wastewater, the CuHCF electrodes removed 85% of NH_4^+ (3.4 to 0.5 mM) with a selectivity >4 versus Na^+ in the presence of other competing cations. These results demonstrate that CuHCF electrodes can be used to selectively remove NH_4^+ from various waters containing multiple ions.



INTRODUCTION

The anthropogenic release of nutrients into the environment can drive eutrophication, threatening the health of aquatic ecosystems.¹ Removal of ammonium from wastewater before its discharge to the environment is particularly needed because it is a major component of the nitrogen species in wastewaters, and nitrogen is the critical limiting nutrient for eutrophication of many receiving waters.² While biological processes are the most common approach for ammonium removal,³ other technologies are being developed with the purpose of ammonium separation and recovery from wastewater, not only to avoid its release but also to enable its reuse. For example, several absorbents can be used for ammonium removal by ion exchange, but these approaches require salty brines to regenerate absorbents for further removal of ammonium in subsequent cycles.^{4–6} Although the use of an ion exchange membrane can avoid the need for regeneration, the selectivity of the membrane for ammonium versus other cations is often low or unknown.^{7–14} Ammonium can be removed from water through its conversion into volatile ammonia by raising the solution pH using chemicals or electrochemical systems and, then, its removal using stripping towers or membrane contactors.^{15–21} These approaches can capture ammonium into valuable salts, such as $(\text{NH}_4)_2\text{SO}_4$, but raising and lowering solution pH can be expensive. Bioelectrochemical systems have also been proposed for ammonium recovery from wastewaters based on using the electrical power produced by microorganisms degrading

organic matter in the wastewater; however, rates of ammonium separation are limited by the low current densities the bacteria produce, and removal is not selective for ammonium.^{22–25}

The use of electrode materials that selectively interact with specific ions by Faradaic reactions offers an alternative method for extracting only certain cations from water.^{26,27} This electrochemical approach has been demonstrated for several different ions in water, but it has not been used to extract ammonium. For example, nickel hexacyanoferrate electrodes were used to selectively remove Cs^+ from wastewater^{28,29} and also preferentially capture K^+ over Na^+ .³⁰ Selective recovery of Li^+ from a brine was achieved using electrode materials developed for lithium ion batteries, such as lithium manganese oxide and lithium iron phosphate.^{31,32} Sodium ion battery electrodes have been used to achieve selective removal of Na^+ over other cations, such as K^+ , Mg^{2+} , and Ca^{2+} .³³ The selectivity of capacitive (i.e., non-Faradaic) electrodes was also investigated with several cations other than ammonium.^{34–36} Although capacitive electrodes have been used for the removal of ammonium, past studies have not examined competitive removal when multiple ions are present.^{37,38}

In this study, we developed an electrochemical system to selectively remove ammonium from wastewaters using copper

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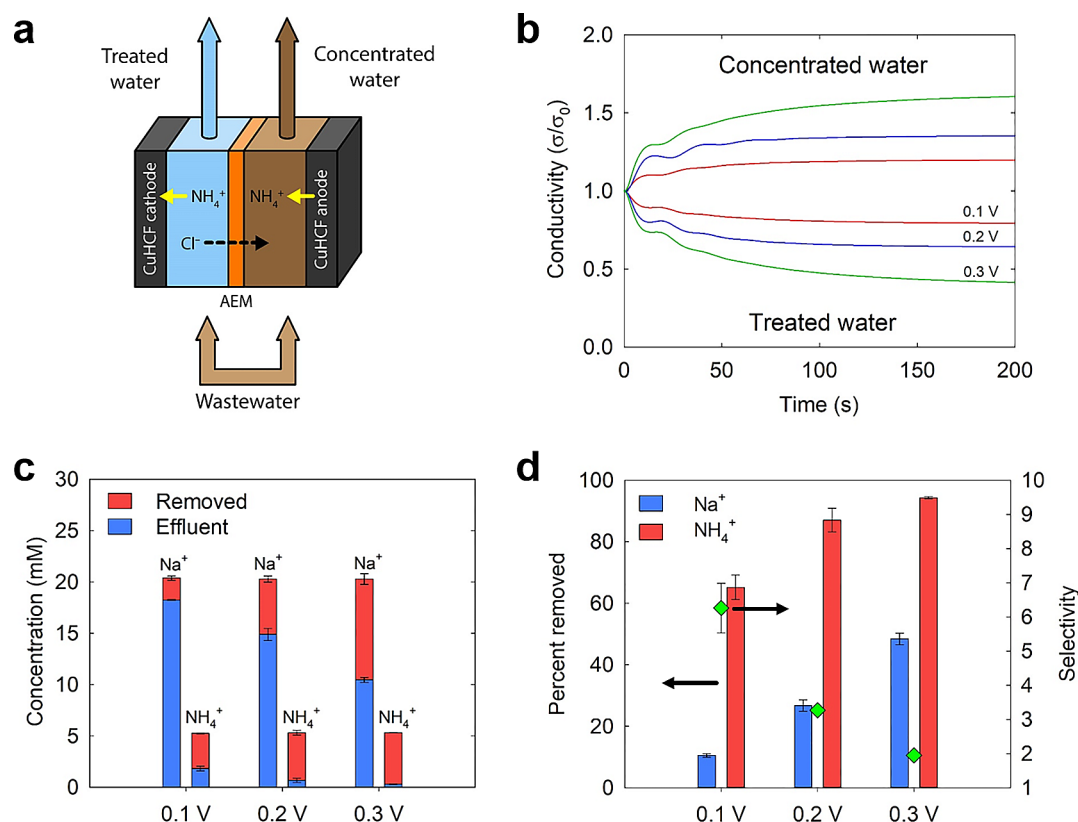


Figure 1. (a) Schematic of the system for ammonium removal using two copper hexacyanoferrate (CuHCF) battery electrodes in two channels divided by an anion exchange membrane (AEM). (b) Conductivity profiles of treated and concentrated waters (synthetic wastewater containing 20 mM NaCl and 5 mM NH₄Cl) recirculated in each channel at the flow rate of 4 mL/min at constant voltages of 0.1, 0.2, and 0.3 V. (c) Concentration and (d) percent removed and selectivity of Na⁺ and NH₄⁺ as a function of the cell voltage. Error bars show the range from duplicate experiments.

hexacyanoferrate (CuHCF) battery electrodes. Electrodes containing Prussian Blue analogues, such as nickel or copper hexacyanoferrate, have been examined primarily for their use with different electrolytes in batteries.³⁹ Electrochemical analysis based on cyclic voltammetry has shown reversible charge and discharge cycles for aqueous electrolytes containing Li⁺, Na⁺, K⁺, or NH₄⁺ over a potential range of 0.0 to 1.4 V (vs standard hydrogen electrode, SHE). Each cation was captured and released to solution over a different potential range in cyclic voltammograms. For a CuHCF electrode, the midpoint potential for Na⁺ was 0.77 V vs SHE, while the midpoint potential for NH₄⁺ was 1.02 V. The different potential for each cation was likely due to the ions having different Stokes radii (NH₄⁺: 0.125 nm; Na⁺: 0.183 nm).^{39,40} Given that electrochemically driven intercalation of NH₄⁺ by CuHCF occurred at a more positive reduction potential,³⁹ we hypothesized that CuHCF would preferentially remove NH₄⁺ at its optimum electrode potential around 1 V (vs SHE) and, therefore, that NH₄⁺ could be selectively removed from a wastewater containing other cations. Using a flow cell previously developed for brackish water desalination (NaCl solutions),⁴¹ we examined the selectivity of CuHCF electrodes for ammonium removal compared to Na⁺ ions using synthetic wastewater containing only Na⁺ and NH₄⁺ and an actual domestic wastewater containing a mixture of inorganic ions and organic matter.

MATERIALS AND METHODS

Electrode Preparation. CuHCF was synthesized using a coprecipitation method as previously reported.^{41–43} Briefly, 100 mL of 0.1 M Cu(NO₃)₂ (Sigma-Aldrich) and 100 mL of 0.05 M K₃[Fe(CN)₆] (J.T.Baker) were simultaneously added at a flow rate of 0.5 mL/min to 50 mL of deionized water under vigorous stirring. The resulting precipitates were collected using a centrifuge after washing several times with deionized water and then dried in a vacuum oven at 70 °C. To make CuHCF electrodes, a slurry composed of CuHCF powder (80 wt %), carbon black (10 wt %, Vulcan XC72R, Cabot), and polyvinylidene fluoride (10 wt %, kynar HSV 900, Arkema Inc.) in 1-methyl-2-pyrrolidinone (Sigma-Aldrich) was loaded onto carbon cloth (1071HCB, AvCarb Material Solutions) using a pipet, followed by drying overnight at 70 °C. Before performing ammonium removal tests, the potential of two CuHCF electrodes was adjusted to 0.8 and 1.0 V versus Ag/AgCl reference electrode in 3 M NaCl (+0.209 V with respect to SHE) in 1 M NH₄Cl (except as noted).

Ammonium Removal Tests. Ion removal tests were performed in a custom-built polycarbonate flow cell (Figure 1a; see Figure S1 for additional information on the cell assembly) consisting of two circular water flow channels (diameter = 30 mm; area = 7.07 cm²) containing fabric spacers (Sefar Nitex 03-200/54, thickness = 120 μm) that were used to provide uniform flow paths, separated by an anion exchange membrane (AEM, Selemion AMV, Asahi Glass, Japan). CuHCF electrodes were placed on the sides of each channel

with graphite foil as a current collector. Each cell outlet was connected to a flow-through conductivity meter electrode (ET908, eDAQ, Australia). The flow cell was first fed by a fresh feed solution until the conductivity meter showed a stabilized value and then recycled during the ammonium removal tests at a flow rate of 4 mL/min. The volume of the recycled solution that filled the flow cell, tubing, and conductivity meter electrode was approximately 1 mL for each side. Constant voltage values of ± 0.1 , 0.2, and 0.3 V were applied to the flow cell using a potentiostat (VMP3, Bio-Logic) for 200 s.

Ammonium removal was examined by two other methods to benchmark their selectivities compared to that of CuHCF with the same solutions. As a representative ion exchange method, cation exchange membranes (CEM, Selemion CMV, Asahi Glass, Japan) were placed onto CuHCF electrodes so that removals were primarily due to the CEM and not the electrode material. Amorphous manganese oxide (MnO_2) was synthesized and used to make electrodes as previously described,⁴⁴ which was tested as an example of nonselective electrode placed in the flow cell instead of the CuHCF electrodes.

Synthetic wastewater was prepared with 5 mM NH_4Cl and 10 or 20 mM NaCl or equimolar (10 mM) NH_4Cl and NaCl . Domestic wastewater was collected from the primary clarifier effluent of the Pennsylvania State University Waste Water Treatment Plant. Wastewater was filtered through a 1.2 μm pore size filter (type RA, MilliporeSigma) and, then, a 0.22 μm pore size filter (type GVWP, MilliporeSigma) prior to ion removal tests ($\text{pH} \approx 8$; conductivity = 1.2–1.3 mS/cm; temperature = 21 °C). The concentration of organic matter was 400 mg/L based on its chemical oxygen demand (COD) analyzed by a colorimetric method (standard method 5220 D) using a DR 3900 spectrophotometer (Hach, CO). The wastewater sample was filtered using a syringe filter (PVDF, 0.45 μm , RESTEK, PA) prior to the analysis.

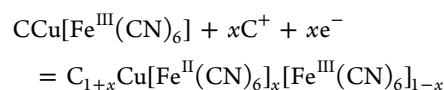
The concentrations of cations before and after the ammonium removal was analyzed with ion chromatography (ICS-1100, Dionex) using Dionex IonPac CS16 (5 \times 250 mm) and CG 16 (5 \times 50 mm) columns. The eluent was 30 mM methanesulfonic acid (Sigma-Aldrich), and the flow rate was 1.0 mL/min. The percent removed was calculated by dividing the amount of removed cations based on the initial concentrations.

Cyclic Voltammetry. Cyclic voltammetry profiles of several salt solutions (1 M NH_4Cl , 1 M KCl , 1 M NaCl , 0.5 M CaCl_2 , and 0.5 M MgCl_2) were recorded in a 3-electrode electrochemical cell at a scan rate of 1 mV/s. A counter electrode was a thick carbon electrode made of Norit SX Plus, and the reference electrode was Ag/AgCl in 3 M NaCl (+0.209 V with respect to SHE).

RESULTS AND DISCUSSION

Selective Ammonium Removal Using a Synthetic Wastewater. The selective removal of NH_4^+ using CuHCF electrodes was initially demonstrated using a synthetic wastewater with a higher sodium concentration compared to ammonium (20 mM NaCl , 5 mM NH_4Cl). Applying a fixed voltage to the cell while the flow in each channel recirculated decreased the solution conductivity in one channel (i.e., treated water) and increased the conductivity in the other channel (i.e., concentrated water). The differences in the conductivities increased when the applied cell voltages went

from 0.1 to 0.2 to 0.3 V (Figure 1b). With electrochemical reactions of CuHCF that can be expressed as



where C stands for cations including Na^+ and NH_4^+ ,^{39,41} treated water was produced from the CuHCF cathode channel due to the cation capture from the solution by CuHCF and Cl^- ion transport to the other side of channel across the AEM. Concentrated water was produced from the CuHCF anode channel as a result of cation release from CuHCF to the solution and Cl^- ion transport from the other side of the channel. After completing a cycle, the voltage was reversed and the effluent streams switched (e.g., the concentrated stream became the diluted stream). In the subsequent cycle, the CuHCF anode released cations that were captured in the previous cycle, and the CuHCF cathode captured cations to produce treated water (see Figure S2 for additional information on cyclic operation, conductivity, and current profiles).

Applying a higher voltage resulted in larger total reductions in Na^+ and NH_4^+ concentrations, with a nearly complete removal of NH_4^+ at 0.3 V (Figure 1c,d). Higher voltages increased the removal of NH_4^+ from $65.2 \pm 4.0\%$ (0.1 V) to $94.3 \pm 0.4\%$ (0.3 V), but the selectivity, defined here as the ratio of percent removed of NH_4^+ to percent removed of Na^+ (also known as a separation factor),⁴⁵ decreased from 6.3 ± 0.7 (0.1 V) to 2.0 ± 0.1 (0.3 V) due to the greatly reduced concentrations of NH_4^+ . The selectivity of the CuHCF electrodes was much higher than that using ion-selective membranes on electrodes or nonselective electrodes. At an applied voltage of 0.2 V, ion-selective membranes (CuHCF-CEM) or nonselective electrodes (MnO_2) produced selectivities <2 compared to 3.3 ± 0.1 obtained using CuHCF electrodes (Figure S3).

Selectivities for Solutions with Different Ammonium and Sodium Concentrations. The impact of ion concentration was further examined by varying the concentrations of Na^+ and NH_4^+ at a constant voltage of 0.1 V. With a synthetic wastewater containing less Na^+ (10 mM NaCl and 5 mM NH_4Cl), we obtained a similar extent of ammonium removal (64%), with a slightly lower selectivity for NH_4^+ (4.8) compared to 6.3 ± 0.7 with 20 mM NaCl and 5 mM NH_4Cl (Figure S4a,b). The use of two other electrode systems (CuHCF-CEM and MnO_2) produced selectivities of <2 (Figure S5). To demonstrate the impact of initial NH_4^+ concentration on selectivity, tests were conducted using a higher and equimolar concentration of NH_4^+ (10 mM of Na^+ and NH_4^+). For this case, the NH_4^+ was removed with a much higher selectivity of 9 at 0.1 V (Figure S6a,b), demonstrating that selectivity was highly dependent on the NH_4^+ concentration.

Impact of Potential. The effect of the potential window on the selectivity was examined using two CuHCF electrode pairs that were prepared at different initial potentials. One pair of electrodes was adjusted to 0.8 and 1.0 V (vs Ag/AgCl in 3 M NaCl ; a more positive potential window), and another pair was adjusted to 0.7 and 0.8 V (a more negative potential window) using 1 M NH_4Cl in a 3-electrode electrochemical cell prior to ammonium removal tests. When a constant voltage of 0.1 V was applied to the flow cell using a synthetic wastewater containing 10 mM NaCl and 5 mM NH_4Cl , we

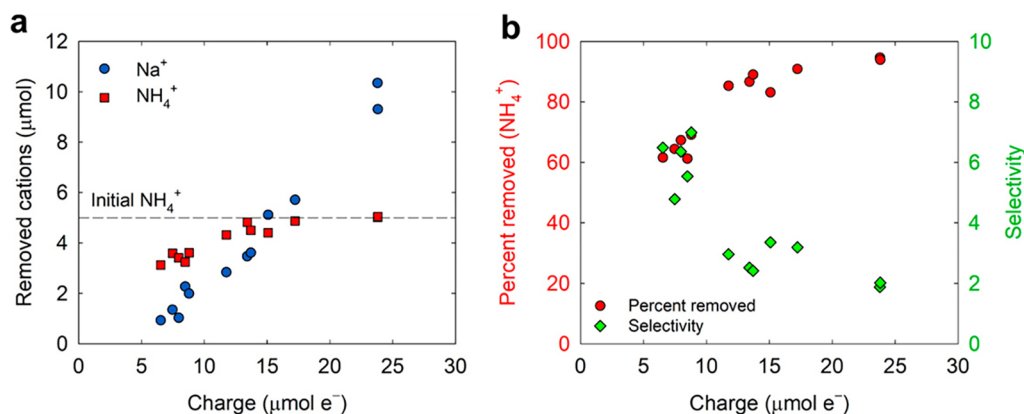


Figure 2. (a) Removed cations and (b) percent removed of NH_4^+ and selectivity as a function of the amount of charge. The initial concentration of NH_4^+ was 5 mM (5 μmol in 1 mL), while that of Na^+ was either 10 or 20 mM.

found similar removal percentages and selectivities for the two pairs of electrodes (Figure S7), indicating that the intercalation of cations by CuHCF was more favorable for NH_4^+ than Na^+ regardless of the potential window.

Cyclic voltammetry profiles obtained using several electrolytes (1 M NaCl, 1 M NH_4Cl , and both 1 M NaCl and 1 M NH_4Cl) further supported the selectivity toward NH_4^+ (Figure S8a). Under the same potential range (0.2–1.1 V vs Ag/AgCl in 3 M NaCl), the use of the electrolyte containing both Na^+ and NH_4^+ produced a profile located close to that of 1 M NH_4Cl with only a marginal shift to that of 1 M NaCl. We also observed that a profile shifted to a more positive potential region by adding NH_4Cl to an electrolyte composed of NaCl, KCl, CaCl_2 , and MgCl_2 (Figure S8b), which suggested that NH_4^+ dictated the potential due to its preferential intercalation. These results were in good agreement with a previous study that investigated the impact of mixed ions (Li^+ , Na^+ , and K^+) on redox potentials of CuHCF electrodes.⁴⁶

Relationship between the Extent of Ammonium Removal and Selectivity. On the basis of data from several ion removal tests, we found that the selectivity was largely dependent on the NH_4^+ concentration. With an initial NH_4^+ concentration of 5 mM, the CuHCF electrode preferentially removed NH_4^+ . As NH_4^+ became depleted in solution, a larger proportion of Na^+ was removed (Figure 2a). A plot of the percent of NH_4^+ removed versus the amount of charge indicated that the increased charge improved the percent removed of NH_4^+ while negatively impacting selectivity (Figure 2b). Under the experimental conditions used here, a constant voltage of 0.2 V provided a good balance between the percent of NH_4^+ removed (>80%) and selectivity (2.9 ± 0.4) compared to Na^+ .

Ammonium Removal from Domestic Wastewater.

The selectivity of NH_4^+ was further examined using an actual domestic wastewater, by measuring the concentrations of the major cations using an applied constant voltage of 0.2 V for 200 s (Figure 3a). NH_4^+ was reduced in concentration to the largest extent (2.9 mM), followed next by Na^+ (1.0 mM), Ca^{2+} (1.0 mM), K^+ (0.3 mM), and Mg^{2+} (0.2 mM), indicating that the CuHCF electrodes predominantly captured NH_4^+ . The selective removal of NH_4^+ was also evident based on the percent removal of each ion, with 85% removal of NH_4^+ , compared to less for the other ions (Ca^{2+} , 75%; K^+ , 71%; Na^+ , 20%; Mg^{2+} , 17%). A selectivity of 4.2 was achieved compared to Na^+ and 2.7 when including all other cations. Preferential

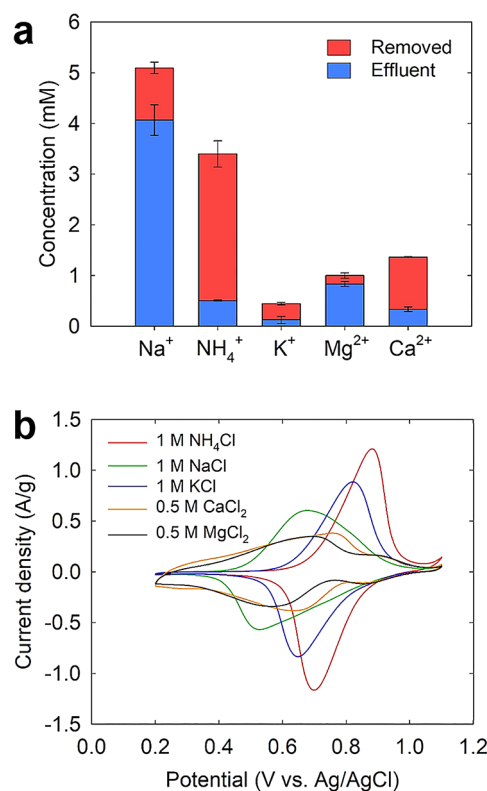


Figure 3. (a) The concentration of removed and effluent cations measured after applying a constant voltage of 0.2 V for 200 s. Error bars show the range from duplicate experiments. (b) Cyclic voltammetry profiles (scan rate = 1 mV/s) of electrolytes containing cations present in wastewater.

NH_4^+ removal was also obtained at a constant voltage of 0.1 V (NH_4^+ percent removed = 61%, selectivity = 4.8 compared to all other cations, Figure S9a) and using synthetic wastewater containing major cations with similar concentrations as in the actual domestic wastewater (NH_4^+ percent removed = 84% and selectivity = 3.5 (0.2 V), NH_4^+ percent removed = 54% and selectivity = 5.2 (0.1 V) compared to all other cations, Figure S9b,c).

The order of ion removal based on percentage followed the same order of the peak potentials obtained using cyclic voltammetry (Figure 3b). When the potential was scanned from positive to negative direction (intercalation), a strong

reduction peak of NH_4^+ was found prior to those of other cations, which suggested that the intercalation of NH_4^+ was favorable over other cations. The reduction peaks of CaCl_2 and KCl were located between 0.6 V and that of NH_4^+ , and in flow cell tests, both showed >70% removals. The peaks for MgCl_2 and NaCl were in potentials more negative than 0.6 V, with percent removals <20%.

Implications for Wastewater Treatment. Not only is the use of CuHCF electrodes highly selective for ammonium compared to other systems (ion-selective membranes or nonselective electrodes),^{8,9,21,37} but also it required less energy than electrochemical systems combined with ammonia stripping.^{18,21} The energy needed using actual domestic wastewater at a constant voltage of 0.2 V was 1.5 kWh/kg-N with 85% nitrogen recovery, which was approximately 7% of the energy needed in a flow-electrode capacitive deionization system using dilute wastewater (21.7 kWh/kg-N, 55.1% nitrogen recovery)²¹ and 17% of that needed in electrodialysis using real urine (8.5 kWh/kg-N, 92.7% nitrogen recovery).¹⁸ The low energy consumption using the CuHCF electrodes was due in part to the use of cell voltage (<0.3 V) that was much lower than those required to increase pH by electrochemical reactions (>1.2 V).

Although we demonstrated that the CuHCF electrodes can be used to selectively remove ammonium from wastewater, there are remaining challenges to improve performance. The selectivity toward NH_4^+ decreased against all cations compared to only Na^+ , which was due to the presence of Ca^{2+} and K^+ in the domestic wastewater. While the effect of these competing ions on ammonium removal was minimal because of low concentrations (<1 mM) compared to that of ammonium (>3 mM), the use of CuHCF electrodes will be best suited for wastewaters with relatively low Ca^{2+} and K^+ contents. We also observed that treated wastewater had a light yellowish color after completing a cycle, which was likely due to dissolution of CuHCF under mildly basic condition of domestic wastewater.⁴⁷ This dissolution was minimal if the pH was reduced below 7, indicating that pH adjustments could be needed for practical applications of alkaline wastewaters. In addition, a concentrated wastewater generated in the other channel will require additional separation steps to further concentrate and remove ammonium. One solution to minimize the volume of concentrated wastewater could be to use a lower flow rate for the concentrate solution than the treated solution. With these technological advancements, our approach could represent an effective method for the selective removal of ammonium from various waters, including domestic wastewater, with low energy consumption.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.8b00334.

Detailed information on the flow cell assembly, cyclic operation, ion removal test results depending on the concentration, voltage, configuration, and initial electrode potential and cyclic voltammetry obtained using mixed ions (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: blogan@psu.edu. Phone: +1-814-863-7908. Fax: +1-814-863-7304.

ORCID

Taeyoung Kim: 0000-0003-0346-5519

Christopher A. Gorski: 0000-0002-5363-2904

Bruce E. Logan: 0000-0001-7478-8070

Notes

The authors declare no competing financial interest.

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