Recovery of Ammonium and Phosphate using Battery Deionization in a Background Electrolyte

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Water Impact Statement

Recovery of nitrogen and phosphorus can not only prevent eutrophication of waters but also provide nutrient-enriched streams. An electrochemical cell containing cation-selective electrodes divided by an anion exchange membrane effectively removed a constant mass of ammonia, but there was less effective removal of phosphorus. The enrichment of ammonia in the concentrated stream will enable its more effective recovery in a side-stream process.

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Recovery of Ammonium and Phosphate using Battery Deionization in a Background Electrolyte

Moon Son [a], Benjamin L. Aronson [a], Wulin Yang [a], Christopher A. Gorski [a], Bruce E. Logan [a,*]

[a] Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA 16802, USA

* Corresponding author. Email: blogan@psu.edu; Tel.: +1-814-863-7908

Abstract

Ammonium ions can be effectively removed from water using electrochemical processes such as battery electrode deionization (BDI), but previous tests have examined removal in the presence of competing ions (e.g. sodium). The recovery of NH_4^+ was examined here in the absence and presence of a relatively inert background electrolyte ($MgCl_2$, 10 mM) added to only provide a conductive solution with cations that have minimal intercalation into the copper hexacyanoferrate (CuHCF) electrodes. The capacity of the CuHCF electrodes for NH_4^+ in the presence of $MgCl_2$ was nearly constant at 8.4 ± 1.4 g−NH_4^+/g−electrode (treated stream, 0.3 V) over a range of 10 to 100 mM NH_4Cl. In addition, the energy needed to remove NH_4^+ was constant at <2.4 kWh kg−N. The impact of Cl^- on removal of phosphate ions was also examined, with ~2:1 removal of Cl^- to phosphate ions (Cl:P) at ratios of up to 4:1. Even at very high ratios of >11.5, at least 20% of the anions removed were phosphate ions compared to Cl^-. These results demonstrate that the capacity of the BDI electrodes is relatively independent of the NH_4^+ concentration, and that phosphate is not selectively removed compared to Cl^-.

Keywords: electrochemical cell; battery deionization; wastewater; ammonium recovery; Phosphate recovery

1. Introduction

Nitrogen and phosphorus are contributing factors to eutrophication of waters when they are released to natural water bodies in treated wastewaters, but they are also valuable nutrients that are worth recovering.[1-4] Various physicochemical or biological methods have been developed to recover or remove nitrogen and phosphorus individually or simultaneously from waters.[5-13] Methods used for nitrogen recovery include ion exchange and NH_3 stripping to produce fertilizer such as $(NH_4)_2SO_4$,[11, 14-17] whereas phosphorus is typically recovered through chemical precipitation.[18, 19] The application of a magnesium ammonium phosphate (MAP) crystallization process has enabled simultaneous recovery of ammonium and phosphate from waters.[20-22] The recovered products, MAP hexahydrate ($NH_4MgPO_46H_2O$), commonly called struvite, can be used as a fertilizer.[23, 24] Struvite recovery is typically applied to more concentrated nutrient streams, such as those from anaerobic digestors, and thus there is a need to concentrate nutrients in dilute wastewaters prior to its recovery as struvite.

Electrochemical processes, including capacitive deionization (CDI), electrodialysis (ED), and electro-adsorption (EO) are recently being investigated to concentrate and recover nutrients from wastewater due to their simplicity and effectiveness.[7-12] However, these processes can have relatively high energy demands. For example, typical energy requirements for these electrochemical processes for ammonium recovery are in the range of 4.4–21.7 kWh/kg−N for CDI (initial NH_4^+ of ~3 mM),[7-9] 8.5 kWh/kg−N for ED (initial nitrogen of 286 mM),[11] and 126 kWh/kg−N for EO (initial NH_4^+ of ~4 mM).[10] These are less effective in terms of energy demands for ammonia removal than biological conversion processes (nitrification and denitrification), which are around 1.7 kWh/kg−N.[12] However, unlike electrochemical processes which can recover ammonium from wastewater, biological processes destroy ammonia rather than recover it. These electrochemical processes also do not have good selectivity for ammonium ions in the presence of competing cations at high current densities. For example, the ion selectivity of ammonium over sodium was 2.5 at 3.0 A m^{-2}, but it decreased to 1.0 as applied current density was increased to 17.2 A m^{-2} in CDI tests using activated-carbon flow electrodes.[8]

A new approach based on intercalation of cations into the electrodes, called battery electrode deionization (BDI), was recently developed[25] to achieve selective removal of ammonium (>90% removal) compared to sodium ions (ammonium/sodium selectivity of >9). In addition, the BDI process had a relatively low energy consumption per mass of nitrogen removed (1.5 kWh/kg−N with 0.2 V applied) compared to other electrochemical systems such as CDI, ED, or EO due to its superior ammonium selectivity.[9, 11] The battery electrodes used in the BDI processes, containing copper hexacyanoferrate (CuHCF), showed preferentially intercalation of ammonium ions (hydrated radius: 3.3 Å) over sodium ions (hydrated radius: 3.6 Å) into the interstitial sites of the CuHCF material (estimated diameters of 3.2 to 4.6 Å[26-30]) at ammonium concentrations of $\leq$10 mM.[25] These previous tests on ammonium removal have been conducted either in the presence of a single competing ion (Na^+) or a mixture of ions, but capacity of the CuHCF electrode for ammonium recovery has not been examined over a wider range of ammonium ion concentrations. In addition, previous research on selective removal of ammonium using BDI process has focused primarily on cations,[25] but the fate of the counter anions is also needed to be explored in order to better understand the process. For example, phosphate ions present in wastewater are recoverable and valuable anions, but only chloride ions have been used so far for the simplicity of examining cation removals in previous studies.[25] In the BDI process, anions are transported into the adjacent channel through an anion exchange membrane (AEM) in order to maintain charge balance, while cations are pulled into the CuHCF electrodes and removed. Thus, while ammonium is intercalated at the cathode, anions are removed by their transport into the concentrated solution along with cations released from the counter electrode that were removed in the previous treating cycle. This working principle of the BDI process is drawn to highlight that BDI using a cation-selective electrode is highly selective for certain cations, unlike other electrochemical processes that can remove different cations and anions in more similar proportion.[31-34] Note that the electrode does not directly remove the anions, but instead the anions pass through the AEM in the middle and move into the adjacent channel. The relative removal of phosphate ions compared to the Cl^- ions has not previously been examined in the BDI process for wastewater treatment.

In this study, we examined the ammonium intercalation (removal) capacity of the CuHCF electrodes and the extend of phosphate ion removal in the presence of chloride ions in the BDI process. In order to examine the capacity of the CuHCF electrode for ammonium, without greatly decreasing the conductivity of the solution, a relatively inert background electrolyte ($MgCl_2$) was used at different initial ammonium ion concentrations. $MgCl_2$ was used for the background electrolyte as it was previously shown that Mg^{2+} ions had a very low reactivity compared to ammonium with a CuHCF electrode.[25] The magnesium concentration was fixed at 10 mM to minimize its effect on the removal rate of ammonium. Therefore, the purpose of using 10 mM Mg^{2+} ions is not because Mg^{2+} is typically present at this concentration in wastewaters, but because Mg^{2+} is relatively inert with respect to reactivity with the CuHCF electrode, making it possible to provide a chloride ion based salt that can maintain solution conductivity even if NH_4^+ ion concentrations are greatly reduced. The ammonium concentration was then varied over a range of 10 to 100 mM in BDI tests at a constant applied voltage of either 0.3 or 0.1 V. The fate of phosphate ions during the ammonia removal process was also examined in the presence of more abundant chloride ions in the water by using the relative molar ratio of the chloride ions to dominant phosphate ions (Cl:P ratio). The energy used for the recovery of ammonium and phosphate was evaluated based on the applied voltage and current at various Cl:P ratios.

2. Materials and methods

2.1 Battery electrode fabrication

A co-precipitation method was used to synthesize CuHCF powder as previously reported.[25, 35] Briefly, equal volumes (80 mL) of 0.1 M $Cu(NO_3)_2$ (Sigma-Aldrich) and 0.05 M $K_3[Fe(CN)_6]$ (J.T.Baker) were gently added to deionized (DI) water (40 mL) with stirring. The precipitates were then purified by centrifugation with DI rinsing, and dried overnight in a vacuum oven to produce the CuHCF powder. Afterward, a drop-casting method was used to add the materials to the electrode. A slurry of CuHCF (80 wt%), carbon black (10 wt%, Vulcan XC72R, Cabot), and polyvinyledenefluoride (10 wt%, Kynar HSV 900, Arkema Inc) in 1-methyl-2-pyrrolidinone (Sigma-Aldrich) was loaded onto carbon cloth (0.25 mm thick; AvCarb Material Solutions, 1071 HCB) using a pipette to produce electrodes that contained 4 mg cm^{-2} of CuHCF. The prepared electrodes were heated and dried at 70°C using a vacuum oven to remove the residual solvent.

2.2 Cell construction

The BDI cell consisted of two cylindrical chambers (30 mm exposed diameter, 7 cm^2 effective area) containing two CuHCF electrodes with two water streams pumped into the channels separated by an AEM (106 ± 1 μm thick with an ion exchange capacity of 1.85 mmol/g, Selemion AMV, Asahi Glass).[36, 37] Graphite foil was used as the current collector for the CuHCF electrodes and rubber gaskets were placed between each component in order to prevent leakage of solution. For both water streams, the flow entered one side of the chamber and exited on the far side of each chamber. In order to secure stable water streams, fabric spacers (0.12 mm thick; Sefar Nitex, 03-200/54) were placed between electrodes and AEM. The conductivity of the solution leaving each chamber was monitored using a flow-through conductivity meters (ET908, eDAQ, Australia) and recorded using a data acquisition system (Conductivity isoPod, eDAQ, Australia). Prior to NH_4^+ and phosphate ions removal tests, the potentials of the two CuHCF electrodes were adjusted to 0.6 and 1.0 V (versus Ag/AgCl reference electrodes) in a separate 3-electrode cell (~2 cm long by ~3 cm in diameter) containing working (CuHCF), counter (activated carbon), and reference electrode (Ag/AgCl in 3 M NaCl), and a working electrolyte of 1 M NH_4Cl, as previously described.[35]

2.3 Ammonium and phosphate removal tests

Electrochemical removal of NH_4^+ ions by the CuHCF can be expressed as

$$NH_4^+Cu[Fe^{III}(CN)_6] + xNH_4^+ + xe^- = NH_4^+{}_{1+x}Cu(Fe^{II}(CN)_6)_x[Fe^{III}(CN)_6]_{1-x} \qquad (1)$$

where NH_4^+ ions are reversibly pulled into or released from the CuHCF cathode material.

In order to determine the removal capacity of the CuHCF electrode for NH_4^+ ions, Mg^{2+} ions were used as background ions due to their relatively low reactivity compared to NH_4^+ with CuHCF electrode.[25] With the fixed $MgCl_2$ concentration of 10 mM, NH_4Cl concentrations were varied from 10 to 100 mM at a constant applied voltage of either 0.3 or 0.1 V. The removal of ammonium (10 mM) was also examined in the absence of the $MgCl_2$ electrolyte.

Five different solutions were synthesized based on different chloride:phosphorus (Cl:P) ratios and ionic strengths using NaCl, NH_4Cl, and $NH_4H_2PO_4$ salts, with each solutions designated as R-x, where x indicated the ratio of Cl:P (1, 4, 11.5 and 24), or the absence of phosphorus (R-0)

(Table 1). The Cl:P ratio was a molar ratio of chloride ion (Cl^-) to phosphate ions, where phosphate anions are present as different chemical species as a function of the pH and their pKa's ($H_2PO_4^-$, pK_a=2.1; HPO_4^{2-}, pK_a=7.2; PO_4^{3-}, pK_a=12.4).[38] Based on the solution pH in the BDI tests during the operation, from pH 5 to 7, the predominant phosphate ion was $H_2PO_4^-$, with lesser concentrations of HPO_4^{2-}. In addition, NH_4^+ is the dominant nitrogen species at that working pH of 5−7 since a pH >9 is required to convert it to NH_3.[9]

The NH_4^+ concentration was maintained at 5 mM in all solutions, except as noted. In experiments to test for the possible formation of struvite ($NH_4MgPO_46H_2O$), 5 mM $MgCl_2$ was additionally added to the R-11.5 and R-24 solutions. The ionic strength of solution was calculated as

$$I = \frac{1}{2}\sum_{i=1}^{n} C_i Z_i^2 \tag{2}$$

where C_i is the molar concentration of each ion (mol L^{-1}), Z_i is the charge number of the ion, and one half accounts for the double counting of both cations and anions.

Table. 1 The Cl:P ratios, ionic strengths, and compositions of the solutions examined for phosphorus removal.

Name	Cl:P ratio	Ionic strength (mM)	Concentration (mM)		
			NaCl	NH_4Cl	$NH_4H_2PO_4$
R-1	1	15	0	2.5	2.5
R-4	4	9	0	4	1
R-11.5	11.5	33	20	3	2
R-24	24	29	20	4	1
R-0	N/A	25	20	5	0

Prior to each experiment, the BDI electrodes were stabilized by flowing the solution through the cell. Once the conductivity profile of the cell effluent was stabilized, a close-loop with 1 mL of volume used to recycle the solution through the cell at a flowrate of 4.0 mL min^{-1}.[25] A constant voltage of either 0.1 or 0.3 V was applied for 200 s using a potentiostat (VMP3, Bio-Logic). The solution pH was measure after the operation using pH strips (MColorpHast^{TM}, Millipore Sigma).

The current profiles obtained in each test were recorded in order to calculate the energy consumption (E_C, kWh) of the cell as

$$\mathrm{E_C} = \int_0^T V\,I\,dt \tag{3}$$

where V is the cell voltage, I is the current, and T is the operation time. The energy consumption of nitrogen (kWh/kg−N) and phosphorus (kWh/kg−P) were calculated by dividing the energy consumption during operation by the mass removed of each substance.

The concentrations of Na^+ and NH_4^+ were analyzed using ion chromatography (ICS-1100, Dionex) using Dionex IonPac CS16 (5 × 250 mm) and CG 16 (5 × 50 mm) columns. Methanesulfonic acid (30 mM, Sigma-Aldrich) was used as the eluent at a flow rate of 1.0 mL min^{-1}. The concentration of total phosphate ions was measured by the Molybdovanadate Test 'N Tube™ Method (Hach, TNT Kit, Total Phosphate, High Range). The Cl^- removal was calculated on the assumption that the total cation removed (NH_4^+ and Na^+) was equal to the sum of the anions (phosphate ions and Cl^-) removed.

3. Results & Discussion

3.1 Ammonium removal capacity

A schematic of the main ions in the BDI process is shown in Fig. 1a, along with a representative plot of the conductivity profiles in the concentrated and treated water channels (Fig. 1b). In this process anions such as Cl^- and phosphate ions are transported into the adjacent channel (right-side in cycle 1) through an AEM in order to maintain charge balance, while cations such as NH_4^+ and Na^+ ions are pulled into the CuHCF cathode (left-side electrode) and removed. Thus, in cycle 1, the left-side channel produces the desalinated water, while the concentrated or brine stream is generated in the right-side channel. The cations being released into the concentrated stream was the cations intercalated into the electrode in the previous cycle. In the subsequent cycle (cycle 2), the direction of the treated and concentrated streams was switched since the voltage was applied in the opposite direction. The CuHCF anode (previously cathode) on the left-side is now releasing (previously intercalated) cations into the concentrated stream. Thus, the BDI system is a semi-continuous process as it can generate both treated and concentrated streams at the same time with 50% water recovery. The conductivity decreased more rapidly when a constant voltage of 0.3 V was applied, compared to that using 0.1 V (Fig. 1b).

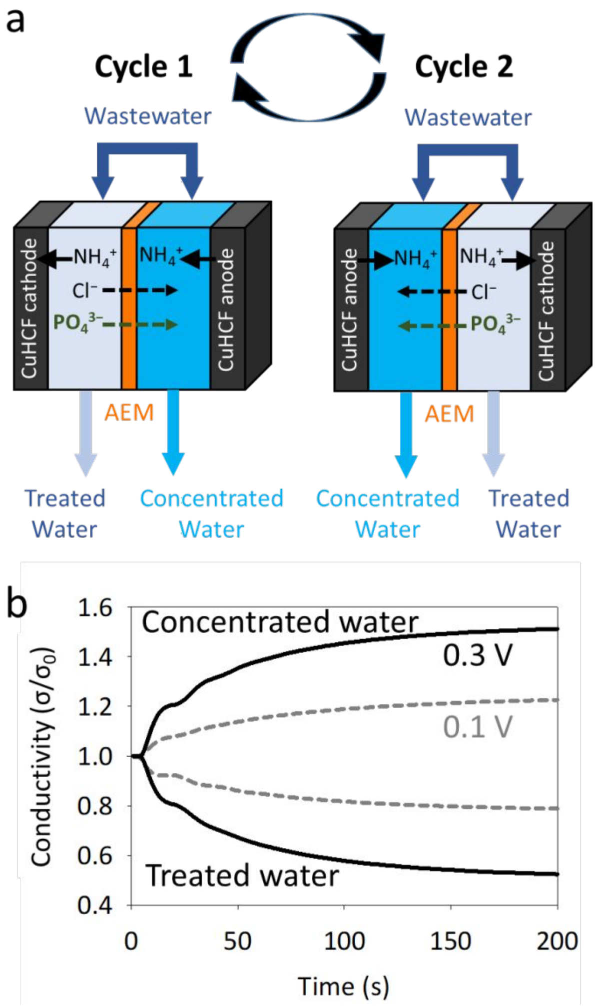

Fig. 1 (a) Schematic of an electrochemical cell using selective battery electrodes, copper hexacyanoferrate (CuHCF), in two channels divided by an anion exchange membrane (AEM). (b) Representative conductivity profiles of treated and concentrated waters at constant voltages of 0.3 or 0.1 V for 200 seconds using synthetic wastewater (R-24 in Table 1).

The addition of 10 mM background electrolyte into the test solution containing 10 mM of NH_4^+ increased NH_4^+ removal due to the higher conductivity of the solution (Fig. 2). In the presence of $MgCl_2$ there was essentially complete removal of NH_4^+ at an applied voltage of 0.3 V (10 mM), compared to 9.9 ± 0.1 mM in its absence (Fig. 2a). At 0.1 V, 5.3 ± 0 mM of NH_4^+ was removed in the presence of 10 mM of $MgCl_2$ compared to 3.9 ± 0.9 mM in its absence (Fig. 2b). The concentration of Mg^{2+} was not substantially altered (<1 mM) in all tests, consistent with a previous report showing a low removal rate of Mg^{2+} by the CuHCF electrode.[25] Thus, the use of relatively inert background electrolyte, Mg^{2+}, enabled a more meaningful assessment of the mass capacity of the electrode since it could provide a background solution conductivity during these tests.

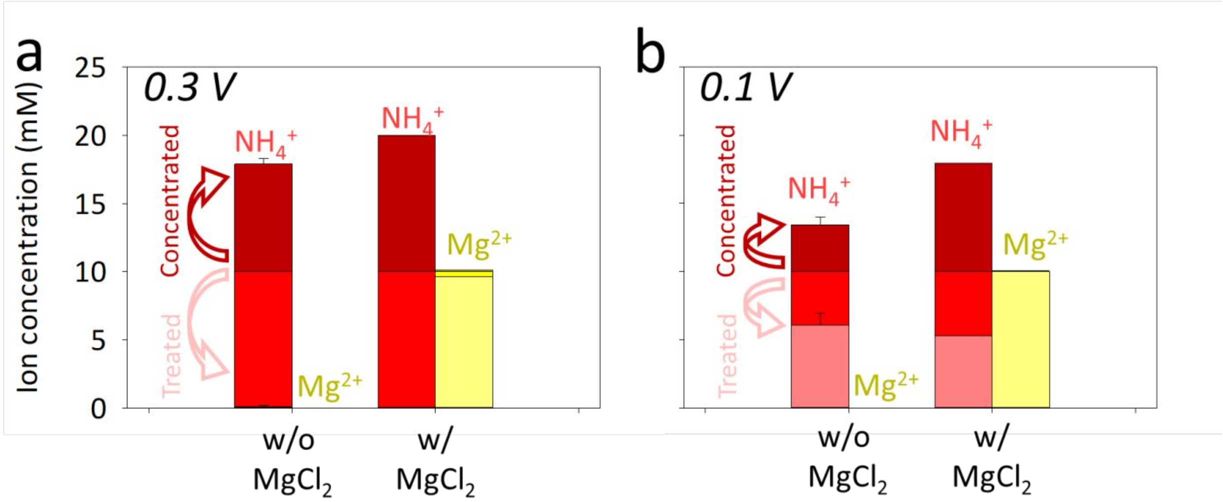

Fig. 2 Concentrations of NH_4^+ and Mg^{2+} (initial concentrations of 10 mM) of the feed, treated, and concentrated streams at an applied constant voltage of (a) 0.3 V or (b) 0.1 V.

When the concentration of NH_4^+ was increased from 10 to 100 mM in the presence of a 10 mM background electrolyte of $MgCl_2$, the concentration of NH_4^+ removed was nearly constant. For example, 10 mM NH_4^+ was removed at a starting concentration of 10 mM, whereas 11 mM of NH_4^+ was removed at an initial concentration of 100 mM, at an applied voltage of 0.3 V (Fig. 3a). Based on the measured removals over the range of 10 to 100 mM NH_4^+, the mass capacity of the electrode was 8.4 ± 1.4 g–NH_4^+/g–electrode (Fig. 3c), with the same amount of ammonium ion (8.3 ± 1.2 g–NH_4^+/g–electrode) released back into the concentrated stream. The concentration of Mg^{2+} in this tests was also altered by <1 mM.[25]

At a lower applied voltage of 0.1 V, the ammonium removed was again very similar over the range of initial ammonia concentrations, although there was less overall total removal due to the lower applied voltage (Fig. 3b). For example, 5 mM NH_4^+ was removed at a starting concentration of 10 mM that was ~50% of the amount removed at 0.3 V. Although more NH_4^+ was removed as the initial concentration was increased up to 100 mM, lower NH_4^+ removal was found at 0.1 V (10 mM at the initial concentration of 100 mM) compared to that of 0.3 V (11 mM at the initial concentration of 100 mM). The mass capacity of the CuHCF cathode (treated stream) was 4.0 ± 1.2 g−NH_4^+/g−electrode at the applied voltage of 0.1 V (Fig. 3c). The greater mass capacity of CuHCF electrode at 0.3 V was due to the greater current flow through the system. This larger current would increase the rate of the reaction and the mass of ions removed, resulting in the greater NH_4^+ removal of the CuHCF electrode at 0.3 V. The measured ammonium released back into the solution (5.2 ± 0.7 g−NH_4^+/g−electrode) was measured to be somewhat higher than that removed (4.0 ± 1.2 g−NH_4^+/g−electrode), likely due to maintaining a set potential of the electrode between cycles, intercalated more NH_4^+ that were released into the next cycle. This discrepancy of the mass capacity between two streams was not found at an applied voltage of 0.3 V because most of the active sites was already filled and thus additional NH_4^+ could not be removed in between cycles.

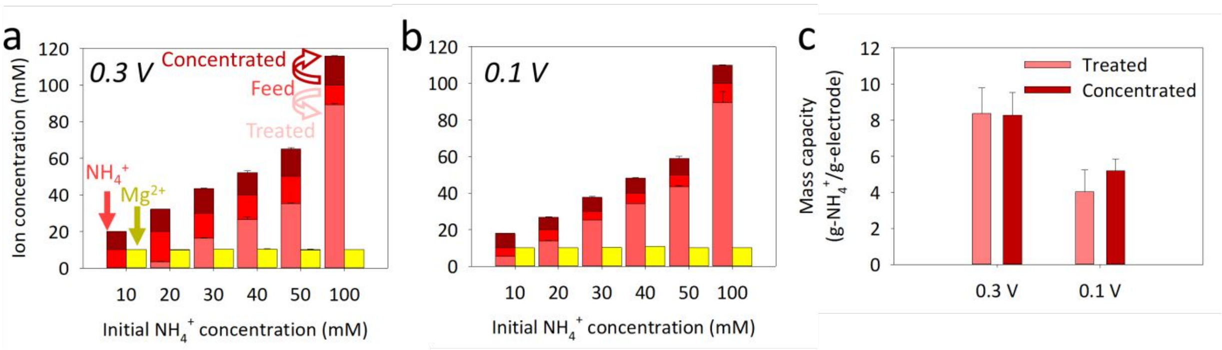

Fig. 3 Ion concentration of ammonium and magnesium of the feed, treated, and concentrated streams when the constant voltage of (a) 0.3 V or (b) 0.1 V was applied. (c) The mass capacity of

CuHCF electrode toward ammonium (g–NH_4^+/g–electrode) as a function of the constant applied voltage.

3.2 Phosphate removal

Chloride ions were preferentially removed in the presence of both Cl^- and phosphate ions, with the phosphate ions removal inversely proportional to the Cl^- concentration in the solution (Fig. 4a). When the Cl:P ratio was 1, 72% of the initial phosphate ions was removed (1.8 mM) compared to 100% of the Cl^- ion. As the Cl^- ion concentration was increased, the removal rate decreased with only 8% removed at a Cl:P ratio of 11.5 (0.2 mM phosphate ions removed). At the highest Cl:P ratio of 24, there was only minimal (4%) phosphate ions removal. This preferential Cl^- ion removal was impacted mostly by the ion's mobility in water and in the membrane, and the relatively higher concentrations of Cl^- than phosphate ions used here to represent conditions in typical domestic wastewaters. The diffusion coefficient of the Cl^- ion (20.3×10^{-6} cm^2 sec^{-1}) is more than two times that of the phosphate ions (8.5×10^{-6} cm^2 sec^{-1} for $H_2PO_4^-$, 7.3×10^{-6} cm^2 sec^{-1} for HPO_4^{2-}, and 6.1×10^{-6} cm^2 sec^{-1} for PO_4^{3-}).[39] Thus, even when the two ions were added at the same concentration, there was greater removal of the Cl^- anion due to its higher diffusion coefficient. As the Cl:P ratio was increased to >4, the relative removal of Cl^- versus phosphate ions increased to > 2:1, which indicated the preferential removal of Cl^- was greater than the differences between the concentrations of the two anions (Fig. 4b). However, when the Cl^- concentrations in the solution were very high relative to that of phosphate ions (Cl:P ratios from 11.5 to 34), the removal ratio of Cl^- and phosphate ions was approximately constant at ~5:1, indicating that at high concentrations of Cl^- this ratio is maintained at this value. This higher removal of Cl^- over the phosphate ions (~5:1) than the difference in the diffusion coefficient (<3:1) could likely be explained by the difference in the size of each anion. For example, the Stokes' radius of phosphate ions (0.256 nm for $H_2PO_4^-$, 0.323 nm for HPO_4^{2-}) is more than two times larger than that of Cl^- ions (0.121 nm).[40] Therefore, smaller Cl^- ions can should pass more easily through the AEM than phosphate ions. The difference in charge of Cl^- and phosphate ions can affect the total number of anions removed but less affect the relative removal of each ion.

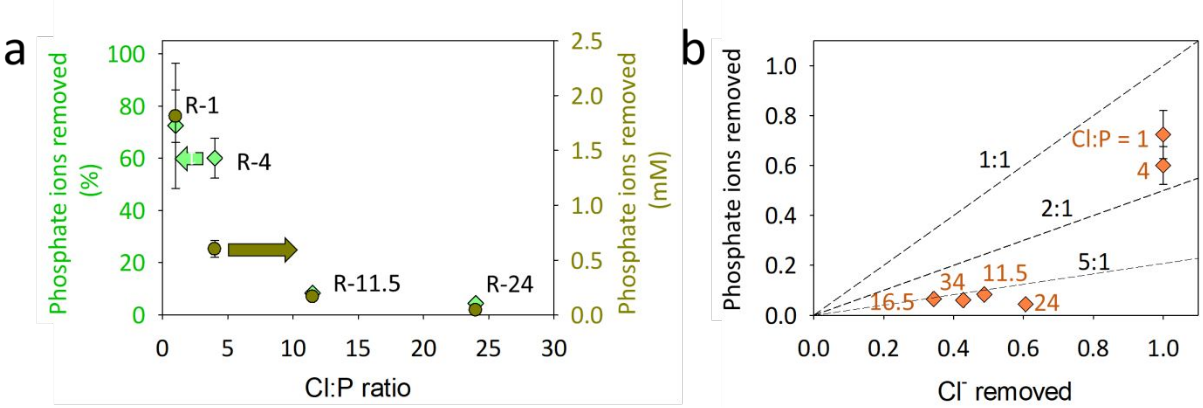

Fig. 4 (a) The removal of phosphate ions in terms of percent (trapezoid, green) and molar concentration (circle, dark yellow) as a function of chloride/phosphorus (Cl:P) ratio. The name of the synthetic wastewater (or Cl:P ratio) used is indicated next to each point. (b) Removed chloride and phosphorus concentrations compared to the initial concentrations. The Cl:P ratio of the synthetic wastewater used was given next to each data point. The numbers associate with the dash lines indicate the removal ratio of Cl^- over phosphate ions. The constant voltage of 0.3 V was applied.

The addition of Na^+ combined with a higher solution ionic strength (which increased the solution conductivity) increased NH_4^+ removal. Na^+ was added in two tests (20 mM) to increase the ionic strength, with higher Cl:P ratios (R11.5 and R-24), without changing the total amount of NH_4^+ (5 mM) at an applied voltage of 0.3 V. A control experiments was also conducted using 20 mM Na^+ with no phosphate ions (R-0) (Table 1). In these higher ionic strength solutions, 100% of NH_4^+ was removed along with 35 ± 3% of Na^+ (Figs. 5 and S2). This improved NH_4^+ removal of 100%, compared to that of >80% at low Cl:P ratio of 1 or 4, was attributed to the increased ionic strength by adding 20 mM of NaCl salt (Fig. 5 and S1), which enabled more current flow through the system. Although some Na^+ ions were also removed, the CuHCF electrodes will preferentially remove NH_4^+ and then Na^+ will be removed due to the higher NH_4^+ selectivity of the electrodes and the low concentration of NH_4^+ ions. For example, <10% of Na^+ was removed when NH_4^+ removal was ~60% (0.1 V) whereas ~40% of Na^+ was removed when 100% of NH_4^+ was removed (0.3 V) (Fig. S2).

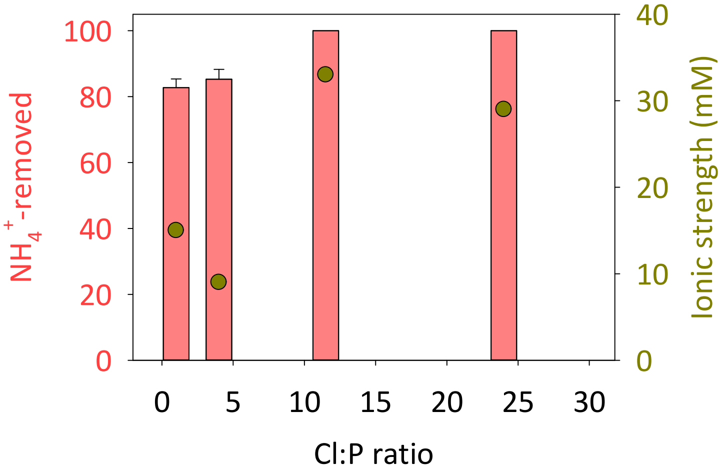

Fig. 5 Ammonium removal (%) as a function of the Cl:P ratio at an applied voltage of 0.3 V (red bar). The relevant ionic strength (mM) of each solution used (R-1, R-4, R-11.5, and R-24) is shown along the ammonium removal (dark yellow circle).

3.3 Struvite formation

The possibility of directly achieving formation of struvite ($NH_4MgPO_46H_2O$), and thus NH_4^+ removal via precipitation, was further evaluated by adding Mg^{2+} ions (5 mM) at the same ratio as NH_4^+ to the two solutions (R-11.5 and R-24). Addition of this amount of $MgCl_2$ salt increased the Cl:P ratio to 16.5 (previously R-11.5) or 34 (previously R-24). About 6% of phosphate ions was removed at the Cl:P ratio of 34, which was slightly higher than that obtained at the lower

Cl:P ratio of 24 (4% removal), likely due to a small amount of struvite formation (Fig. S3). The lack of extensive struvite formation was likely limited by the solution pH of ~5 in the concentrated stream, as it is well known that struvite formation is favorable only at alkaline pHs.[20-22] In a BDI cycle, the solution pH of the concentrated stream was typically between pH 5 to 7 (0.3 V to 0.1 V) while that of the treated stream was relatively constant at pH ~7.

3.4 Energy consumption and implications for wastewater treatment

The energy consumption for NH_4^+ removal in these BDI tests expressed on the basis of the NH_4^+ removed increased slightly as a function of the Cl:P ratio, from 1.1 ± 0.1 kWh kg−N (Cl:P ratio of 1) to 2.4 ± 0.1 kWh kg−N (Cl:P ratio of 24) (Fig. 6). When the energy consumption was normalized to the amount of phosphorous removed, then the amount of energy required was quite variable as the amount of phosphate ions removal was not correlated with the overall desalination performance. For example, the energy required was 1.3 ± 0.2 kWh kg−P at a Cl:P ratio of 1, whereas it was 117 ± 27 kWh kg−P at the Cl:P ratio of 24. Thus, the performance of the system was better related to NH_4^+ removal rather than phosphate ions removal.

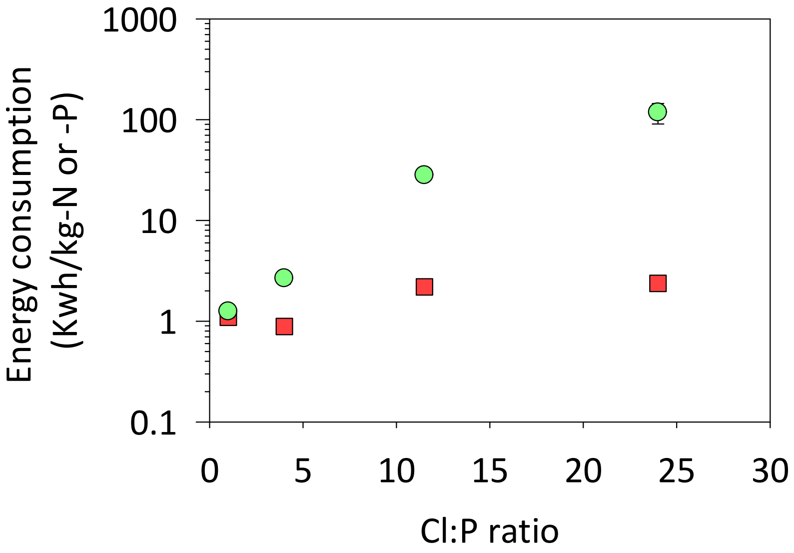

Fig. 6 Energy consumption (kWh) to remove either nitrogen (kg−N) or phosphorus (kg−P) as a function of chloride/phosphorus (Cl:P) ratio.

Although our previous study showed constant charge efficiency of ~80% over 50 cycles of operation using CuHCF electrodes for water desalination (influent = 50 mM NaCl, flow rate = 0.5 mL min^{-1}, voltage range = ±0.3 V, constant current = 5.7 A m^{-2}, double-stacked BDI cell),[35] the stability of the BDI process for long-term operation at larger scales should be conducted for more practical applications relative to wastewater treatment. The stability of the CuHCF electrode will depend on the feed compositions and the operating conditions. For example, when a higher feed concentration (50 mM NaCl) was used at the lower flow rate (flow rate = 0.5 mL min^{-1}) with the narrow voltage range (±0.3 V, constant current = 5.7 A m^{-2}, double-stacked BDI cell), a constant charge efficiency of ~80% was measured over 50 cycles of operation.[35] In contrast, when a lower feed concentration (20 mM NaCl) was tested at the higher flow rate (flow rate = 20.0 mL min^{-1}) with the wider voltage range (±0.6 V, constant current = 5.0 A m^{-2}, single-stacked BDI cell), only ~50% of retention capacity was been reported over the same 50 cycles of operation.[41]

Recent studies on electrochemical processes such as CDI for water desalination have revealed that energy consumption and efficiency of the electrochemical process must be considered together with the feed concentration and extent of ion removal for fair comparison to other processes.[42, 43] In that context, the higher removal rate (~100%; initial NH_4^+ of 5 mM) at the lower energy consumption (<2.4 ± 0.1 kWh kg–N) of this BDI process due to the high selectivity for NH_4^+ of the CuHCF electrodes could render it more suitable for wastewater treatment than other electrochemical processes such as CDI (<90% removal; initial NH_4^+ of ~3 mM; 4.4–21.7 kWh/kg–N[7-9]).

The BDI process did not raise the solution pH to be suitable for the direct formation of struvite (an alkaline pH is needed). However, an NH_4^+ and phosphate ion enriched stream (concentrated stream) was generated that could facilitate struvite formation through post-treatment pH adjustment. Therefore, NH_4^+ and phosphate ions can be recovered by forming struvite more efficiently in the concentrated stream through pH adjustment than the original feed water. As struvite formation is generally proportional to the concentrations of NH_4^+ and phosphate ions, the concentrated stream could be used to form struvite with higher efficiency than using the original feed stream.

4. Conclusions

A BDI system with NH_4^+ selective CuHCF electrodes was tested in order to determine its mass capacity toward NH_4^+ in the presence of a relatively non-competing cation (Mg^{2+}), as well as its ability for additional recovery of phosphate ions. The mass capacity of the electrodes for ammonium ion removal was 8.4 ± 1.4 g–NH_4^+/g–electrode at an applied voltage of 0.3 V, over a range of initial NH_4^+ concentrations of 10 to 100 mM, in a fixed background electrolyte of 10 mM $MgCl_2$. However, there was limited phosphate ions removal under conditions typical of municipal wastewaters (the Cl:P ratios of >30).[44, 45] The removal of phosphate ions was dependent on the concentration of Cl^- ions, as chloride ion removal was more favorable compared to phosphate ions. At very high Cl:P ratios of >11.5, the concentration of phosphate ions recovered was at least ~20% of that of Cl^-. The energy required for NH_4^+ removal was from 1.1 ± 0.1 kWh kg–N (Cl:P ratio of 1) to 2.4 ± 0.1 kWh kg–N (Cl:P ratio of 24). These results show that NH_4^+ removal can be slightly improved by using more conductive solutions, but phosphate ions removals will in general be low due to the selective removal and higher concentrations of Cl^- compared to phosphate ions.

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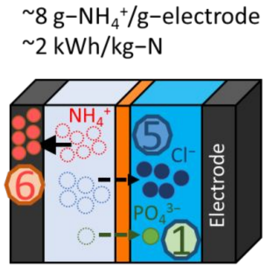

The electrochemical cell containing ammonium selective battery electrodes can be an effective process for recovering ammonium, but not phosphate, from solutions due to its high mass capacity for ammonium ions, with a low energy demand.