



Electrochemically driven extraction and recovery of ammonia from human urine



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ABSTRACT

Human urine contains high concentrations of nitrogen, contributing about 75% of the nitrogen in municipal wastewaters yet only 1% of the volume. Source separation of urine produces an ideal waste stream for nitrogen and phosphorus recovery, reducing downstream costs of nutrient treatment at wastewater treatment facilities. We examined the efficiency and feasibility of ammonia extraction and recovery from synthetic and undiluted human urine using an electrochemical cell (EC). EC processing of synthetic urine produced an ammonium flux of $384 \pm 8 \text{ g N m}^{-2} \text{ d}^{-1}$ with a $61 \pm 1\%$ current efficiency at an energy input of $12 \text{ kWh kg}^{-1} \text{ N}$ removed. EC processing of real urine displayed similar performance, with an average ammonium flux of $275 \pm 5 \text{ g N m}^{-2} \text{ d}^{-1}$ sustained over 10 days with $55 \pm 1\%$ current efficiency for ammonia and at an energy input of $13 \text{ kWh kg}^{-1} \text{ N}$ removed. With the incorporation of an ammonia stripping and absorption unit into the real urine system, $57 \pm 0.5\%$ of the total nitrogen was recovered as ammonium sulfate. A system configuration additionally incorporating stripping of the influent headspace increased total nitrogen recovery to 79% but led to reduced performance of the EC as the urine ammonium concentration decrease. Direct stripping of ammonia (NH_3) from urine with no chemical addition achieved only 12% total nitrogen recovery at hydraulic retention times comparable with the EC systems. Our results demonstrate that ammonia can be extracted via electrochemical means at reasonable energy inputs of approximately $12 \text{ kWh kg}^{-1} \text{ N}$. Considering also that the hydrogen generated is worth $4.3 \text{ kWh kg}^{-1} \text{ N}$, the net electrical input for extraction becomes approximately $8 \text{ kWh kg}^{-1} \text{ N}$ if the hydrogen can be used. Critical for further development will be the inclusion of a passive means for ammonia stripping to reduce additional energy inputs.

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1. Introduction

Strict regulations exist for nitrogen discharge from municipal wastewater treatment plants (WWTP). This results in considerable costs at the WWTP level in terms of energy expenditure and material costs for nitrogen removal. The major source of nitrogen in municipal wastewater is urine, accounting for 75% of the total nitrogen load to the WWTP (Larsen and Gujer, 1996) and less than 1% of the sewage volume. Separating urine from this wastewater creates the opportunity for recovery of the ammonia at high concentration, thereby avoiding its energy intensive removal as nitrogen gas, and alleviating losses during transport. Current established technologies for nitrogen removal from nitrogen rich wastewaters

include nitrification/denitrification, direct stripping, and precipitation as struvite (for quantitative N recovery). While each of these technology has an energetic cost, and additional costs for recovering ammonia must be considered against the cost of production. The major process for ammonia production is the Haber–Bosch process, which uses natural gas or oil directly as an energy source at an electrical cost of approximately $10 \text{ kWh kg}^{-1} \text{ N}$ (Maurer et al., 2003). The Haber–Bosch process utilizes natural gas or oil directly, but the cost is represented as electrical here for sake of comparing these technologies with our system described here.

The current approaches for ammonia recovery typically produce chemically combined forms, either struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) or ammonium sulfate through chemical precipitation (Doyle and Parsons, 2002) or stripping (Siegrist, 1996), respectively. These forms deliver limited return on investment due to their low market value. Moreover, substantial chemical addition is often needed e.g., for pH control in stripping, for quantitative nitrogen removal

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through struvite precipitation, or for carbon supplementation during denitrification. Here we investigate an alternative strategy, an electrochemical cell (EC) coupled to a stripping/absorption unit, for selective ammonium removal and recovery from urine. Here ammonia is recovered as ammonium sulfate, but hydrogen production offers an additional high value resource if recovered. This approach was evaluated earlier for ammonia recovery from synthetic and real anaerobic digester effluents (Desloover et al., 2012, 2015). Two recent reports have demonstrated ammonia recovery from urine using a bioelectrochemical system (BES) approach via either a microbial fuel cell (MFC) system (Kuntke et al., 2012), or a microbial electrochemical cell (MEC) system (Kuntke et al., 2014). In contrast to an EC, the BES are driven by current produced through microbial oxidation of organics in the anode.

The applied current in an EC system provides a potential difference between the electrodes high enough to drive water oxidation at the anode (oxygen and protons produced), and water reduction at the cathode (hydrogen gas and hydroxyl ions produced) leading to an acidic anode and basic cathode in the absence of buffer. This current drives electromigration of cations from the anode to the cathode across a cation exchange membrane (CEM). Thus NH_4^+ can be transferred from the anode to cathode where it is converted to NH_3 in the high pH environment where it is easily stripped (along with H_2) using an air flow. Continual removal of the ammonia allows constant flux of ammonium ions from the anode as the TAN concentration gradient remains constant across the membrane. The stripping gas is then passed through an acid trap or other means (such as condensation) where only NH_3 is captured and concentrated as a high purity ammonium product. Here, we used H_2SO_4 as the sorbent delivering $(\text{NH}_4)_2\text{SO}_4$ to quantify the ammonia recovery at laboratory scale.

Approximately 85% of the nitrogen in fresh urine is fixed as urea (Udert et al., 2006). This urea is readily hydrolyzed by ubiquitous urease producing bacteria present throughout collection systems (Udert et al., 2003a). Hydrolysis of one mole of urea releases two moles of ammonia and one mole of carbonic acid (Mobley and Hausinger, 1989) according to Equation (1).



This hydrolysis results in a net increase in the pH and conductivity of the urine, creating conditions that allow spontaneous precipitation of calcium, magnesium, phosphate, and ammonium ions present in the urine (Udert et al., 2003a). The extent and distribution of these precipitates will vary depending on the concentration of these ions in the urine, which can vary person to person, or vary in the dilution water by location. The degree of dilution by flushing will also affect precipitation dynamics. Formation of these precipitates throughout the collection system is problematic, and will require modifications in systems intended for low or no flush toilets. Precipitates, particularly those of calcium and magnesium, can also cause problems in EC systems through scaling of the CEM. Optimized precipitation via hydrolysis, upstream of EC, may provide a more suitable solution for electrochemical extraction of ammonia, and will be considered here as part of the process line.

The goal of this study was to evaluate the performance of an EC system for ammonia recovery from undiluted human urine under different operational parameters. To our knowledge, electrochemical treatment for ammonia recovery from human urine has not yet been reported. Initial tests were performed with synthetic urine (ammonium carbonate solution with the pH and concentrations of hydrolyzed urine), without any pH adjustment. After key parameters such as HRT and current density impact were established, EC treatment of real, undiluted human urine was evaluated. These results are then compared against the two reported BES

systems.

2. Materials and methods

2.1. Medium composition

A synthetic urine solution was developed from the fresh urine model presented by Kuntke et al. (2013). It was modified to reflect the change in composition that would result from biologically induced hydrolysis of urea and precipitation of salts (presumably struvite, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$; hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$); and calcite, CaCO_3) in a urine collection system (Udert et al., 2003b). Synthetic urine contained (g L^{-1}): $(\text{NH}_4)_2\text{CO}_3$ (27.5), NaCl (4.72), KCl (3.6), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (3.9), KH_2PO_4 (70 mg L^{-1}), and K_2HPO_4 (90 mg L^{-1}). This assumes 97% $\text{P} - \text{PO}_4^{3-}$ removal, and 100% removal of magnesium and calcium during pretreatment. The pH of this solution was 9.1 without adjustment.

Approximately 14 L of fresh human urine was collected over one day from 23 females and 20 males. Urine was pooled, mixed and divided into two batches, A and B, and subsequently stored at 4 °C prior to use (not exceeding 40 days). Batch A was used for System I experiments and batch B was used for Systems II and III experiments. After storage at 4 °C and prior to use as a feedstock, urine batches were pretreated with jackbean urease (Sigma, cat# U1875, St. Louis, MO, USA) at 1 mL (500–800 U) per liter urine to hydrolyze urea and initiate salt precipitation. The urine was incubated for 4–5 days at room temperature without mixing. The extent of hydrolysis was determined from samples taken before and after urease pretreatment for each run and analyzed for the following: total ammonia nitrogen (TAN), total kjeldahl nitrogen (TKN), pH, conductivity, COD, chloride, nitrite, nitrate, phosphate, sulfate, potassium, calcium, magnesium, and sodium. After hydrolysis, precipitates settled and the supernatant was carefully decanted to serve as reactor feed.

2.2. Experimental outline

Before assessing ammonia removal and recovery from real urine, preliminary tests were performed on synthetic urine in a continuously run electrochemical cell to establish an optimal hydraulic retention time and applied current for the electrochemical cell (EC). Three system configurations were subsequently used to assess electrochemical ammonia extraction and recovery on real urine with the incorporation of a stripping/adsorption unit. In system I, the catholyte was recirculated over the stripping column, and gas from the stripping column was transferred to the absorption column via a vacuum pump. System II utilized a second vacuum pump to recover ammonia from the headspace of the anode influent reservoir in addition to the catholyte. In System III the EC was omitted and the hydrolyzed urine was recirculated directly over the stripping column.

2.3. Electrochemical cell and stripping/absorption unit

The EC consisted of two compartments (internal dimensions: $8 \times 8 \times 1.9$ cm, 2 cm wall thickness) made from two square Perspex[®] frames separated by a cation exchange membrane (CEM) (Ultrex CMI-700, Membranes International Inc., USA). A titanium (Ti) electrode coated with iridium mixed metal oxide (Ir MMO) was used as the anode (dimensions: 7.8×7.8 cm; 1 mm thickness; specific surface area $1.0 \text{ m}^2 \text{ m}^{-2}$, Magneto Special Anodes, The Netherlands) and a 316 L stainless steel mesh was used as the cathode (mesh width 564 μm , wire thickness 140 μm , Solana, Belgium). These layers were sandwiched between rubber sheet seals, cut to the frame dimensions to create a liquid tight seal, and

bolted between the two Perspex® frames. The anode was placed 1 cm from the CEM, the cathode was separated from the CEM by a 2 mm thick polytetrafluoroethylene (PTFE) turbulence promotor mesh spacer (ElectroCell, Denmark). Anode, cathode, spacer, and CEM all had a projected surface area of 64 cm². The cathode was used as the working electrode and the anode as the counter electrode. A VSP Multi Potentiostat (Bio-Logic Science Instruments SAS, Claix, France) was used for electrochemical control. The cathodic half-cell potential was measured by a Ag/AgCl reference electrode (assumed +0.197 V vs standard hydrogen electrode (SHE), Bio-Logic Science Instruments SAS, Claix, France) immersed in the cathode compartment. The anode potential was calculated as the difference between the cell voltage and the cathode potential, and was not corrected for ohmic resistance. The stripping/absorption unit materials and construction were identical to the Type 2 unit used in a previous study (Desloover et al., 2012) and a detailed schematic is given there. An important difference here, is that the air flow through the stripping/absorption units was run in an open circuit rather than in a closed circuit (Fig. 1). Further modifications to air flow are described below. The absorption column was filled to 500 mL with 3 M sulfuric acid in these experiments.

2.4. EC and systems operations

For the EC tests, a range of synthetic urine flow rates to the anode and applied currents were tested to assess EC performance at different anodic hydraulic retention times (HRTs) and applied

currents. A solution of 0.1 M NaCl was fed through the cathode at a flow rate of 5 L d⁻¹ (HRT 0.6 h). Anode and cathode were fed continuously and each compartment was internally recirculated at a rate of 6 L h⁻¹ to provide mixing. EC runs were performed under open circuit (OC), and at 10, 30, or 50 A m⁻² for each of the four HRTs tested, for a total of 32 runs. HRT were tested between 2.7 and 12 h. Anode and cathode effluents were sampled four times over a 4–6 h period after steady state (3x HRT) was reached. Anode and cathode influents were sampled at the beginning of each run.

Extraction and recovery of ammonia from real urine was tested under three different system configurations (Fig. 1). In Systems I and II, hydrolyzed urine was fed continuously to the anode at 0.5 L d⁻¹ (6 h HRT), and the catholyte was internally circulated over the stripping unit (thereby increasing the total effective cathode volume to 202 mL). The cathode feed rate was decreased to 0.5 L d⁻¹ (11 h HRT, including the stripping column volume), and again internal recirculation rates for both anode and cathode were 6 L h⁻¹. The stripped gas was circulated countercurrent to the catholyte flow via a vacuum pump (VWR International, Radnor, PA, USA) from the top of the stripping column to the bottom of the absorption column in an open circuit (air flow rate: 2.5–4.5 L min⁻¹). In System I, the anode feed bottle was covered but not gastight. In configuration II the gas from the feed bottle head-space was evacuated via a second vacuum pump (air flow rate: 2.5–4.5 L min⁻¹, open circuit) and combined with the stripping gas flow just prior to the absorption column. Anode influent, anode effluent, cathode effluent and the absorption column were sampled

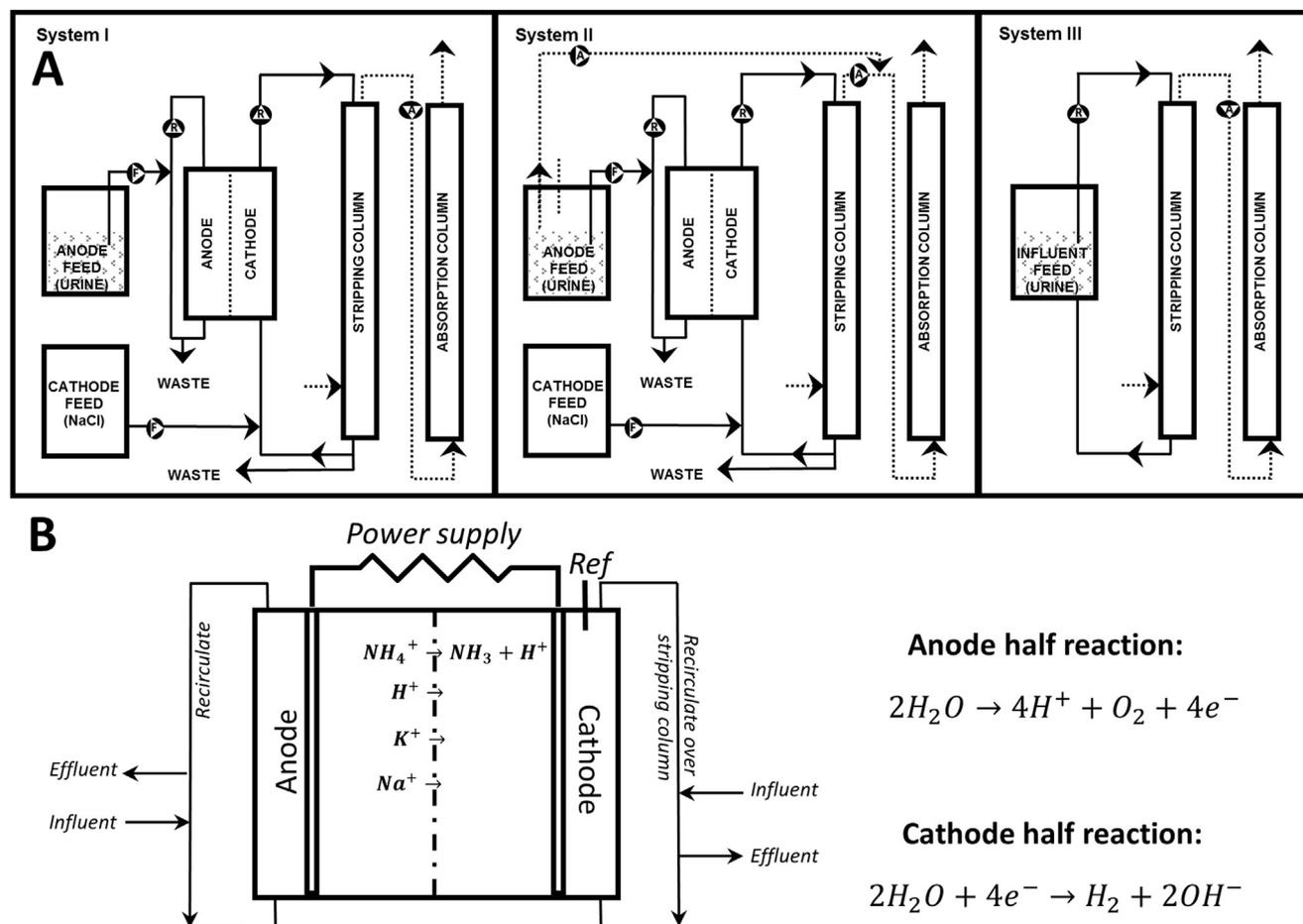


Fig. 1. A: Overview of Systems I, II, and III showing liquid flow (solid arrows) and air flow (dashed arrows) configurations. Pumps: air/vacuum pump (A), feed pump (F), recirculation pump (R); B: detailed schematic of electrochemical unit, "ref" indicates reference electrode placement.

once daily after steady state conditions (3 HRTs) were reached.

In System III, the EC cell was omitted to determine nitrogen recovery from stripping alone. A 900 mL batch of hydrolyzed urine (reserved from urine batch B) was internally circulated from a 1 L bottle at approximately 6 L h^{-1} directly over the stripping column. Stripping gas flow was the same as in System I setup. Samples were taken frequently over 3 days from the influent bottle and the absorption column. Samples from all experiments were stored at 4°C .

2.5. Chemical analyses

Total Kjeldahl nitrogen (TKN) and ammonium (NH_4^+) were measured by steam distillation on a Vapodest 30 steam distillation unit (Gerhardt Analytical Systems, Königswinter, Germany) according to Standard Methods (Clesceri et al., 1998). Sodium, potassium, calcium, and magnesium were measured by flame-atomic adsorption spectrometry (AAS) (Shimadzu AA-6300, Shimadzu Scientific Instruments, Somerset, NJ, USA). Prior to analysis samples were acidified with hydrochloric acid (K^+ and Na^{2+}) or nitric acid (Mg^{2+} and Ca^{2+}), respectively. Additionally 2% of a 1 g L^{-1} lanthanum standard solution (Chem-Lab, Zedelgem, Belgium) was added to Mg^{2+} and Ca^{2+} samples before measurement. Nitrate, phosphate, chloride, and sulfate were measured by a Metrohm 761 compact ion chromatography system (Metrohm AG, Herisau, Switzerland). COD was measured directly using a Nanocolor[®] COD kit (Machery-Nagel GmbH & Co., Düren, Germany).

2.6. Calculations

Ammonium flux, current efficiency (CE), removal efficiency, and power input per kg TAN extracted were calculated for the EC to assess performance in the preliminary tests, and in systems I and II. Power input is reported as kWh and reflects only the electrical input to the EC. Ammonium recovery efficiency was assessed for systems I, II, and III. Ammonia removal efficiencies reflect the efficiency of $\text{NH}_4^+ - \text{N}$ transfer through the EC while ammonia recovery efficiencies reflect efficiency of $\text{NH}_3 - \text{N}$ stripping from the catholyte, thus these are useful in comparing EC performance in different systems. Current efficiency refers to the molar fraction of an ion transferred across the membrane per mole of electrons transferred, and refers to ammonium (NH_4^+) unless otherwise specified. Total ammonia nitrogen (TAN) recovery through the entire system (EC + stripping/absorption) was calculated to compare the performance of different systems (I and II) in terms of nitrogen recovery by performing a mass balance of each system. Removal and recovery capacities were used to compare direct stripping (System III) to the electrochemical extraction (System I). Equations for all calculations are provided in the supplementary materials.

3. Results

3.1. EC performance for ammonium ($\text{NH}_4^+ - \text{N}$) extraction: synthetic urine

Ammonia flux was maximized at high applied current and short hydraulic retention time (HRT) (Fig. 2A). The highest flux, $500 \text{ g NH}_4^+ - \text{N m}^{-2} \text{ d}^{-1}$, was achieved at an HRT of 2.8 h and an applied current density of 50 A m^{-2} . For any set HRT, flux increased with increasing applied current density. Migrational flux is ultimately limited by the applied current density such that as the current is increased, the maximum theoretical migrational flux is increased. Nitrogen flux did not appear to correlate with HRT except for at high applied current density (50 A m^{-2}) where flux correlated negatively with HRT ($R^2 = 0.6$). Demonstrated by the open circuit

runs, ammonia flux due to diffusion alone was on average $55 \pm 15 \text{ g NH}_4^+ - \text{N m}^{-2} \text{ d}^{-1}$, accounting for 4–11% of ammonia flux at HRTs between 2.8 and 8.3 h, and 22% at the 12.4 h HRT. Removal efficiency for ammonium ion was maximized as both applied current and HRT were increased. Removal efficiency had a strong positive correlation with HRT under OC and all CC runs (Fig. 2B), whereas flux appeared to decrease at higher HRT, at least at 50 A m^{-2} . The highest removal efficiency, $86.7 \pm 0.2\%$, was achieved at 50 A m^{-2} and a 8.2 h HRT. Above this HRT the removal efficiencies leveled off at higher applied currents. The lowest removal efficiency, $4.2 \pm 2\%$, was observed under open circuit at an HRT of 2.8 h.

Current efficiency (CE) decreased as both HRT and applied current increased (Fig. 2C) with the lowest CE, $40 \pm 0.1\%$, observed at 50 A m^{-2} , 12.4 h HRT. The highest CE, $108 \pm 21\%$, was observed at 10 A m^{-2} , 2.8 h HRT. CE showed a stronger negative correlation with applied current (regression analysis not shown) than with HRT. The power input required per kg of ammonia removal increased with increasing HRT and applied current (Fig. 2D). The highest input, 19 kWh kg N^{-1} , was observed at 50 A m^{-2} and 12.4 h HRT. The lowest input, 4 kWh kg N^{-1} , was observed at 10 A m^{-2} , 2.8 h HRT.

The synthetic urine solution is strongly buffered by an ammonia and carbonate system provided by the ammonium carbonate. Increasing either the HRT or applied current increases the concentration of protons in the anode and will consume buffer. Increasing both will eventually lead to a sharp decrease in the pH as the buffer capacity of the anolyte is exhausted. This was observed at 8.3 h or 6.3 h under applied current densities of 30 A m^{-2} and 50 A m^{-2} , respectively (Fig. 3B). The substantial pH decrease observed here results in an approximately 10^5 increase in the concentration of protons that then compete with ammonium transfer, thus reducing the CE of ammonia. The drop in pH also corresponded to a plateau in ammonia removal efficiency at these higher applied currents (Fig. 2B), and a pronounced drop in nitrogen flux at 12 h HRT (Fig. 2A). Cathode pH increased from 8.5 ± 0.2 at open current to 11.9 ± 0.1 at 50 A m^{-2} (Fig. 3A). Cell potentials were stable over each run, with an average voltage of 2.6 ± 0.0 , 3.3 ± 0.1 , and $3.8 \pm 0.1 \text{ V}$ at applied current densities of 10, 30, and 50 A m^{-2} respectively.

Ammonia removal efficiency reflects the degree of treatment, as measured by the anode effluent ammonia concentration. A higher removal efficiency corresponds to lower effluent TAN, which means better treatment. Increasing the applied current has a positive effect on both ammonia removal efficiency and flux, but a negative effect on current efficiency. Optimizing the system requires a compromise between minimizing power input and maximizing removal efficiency. At least 30 A m^{-2} is required to reach maximal removal efficiency (Fig. 2B). In this range, HRT above 8 h leads to lower flux, lower CE, and higher power input, while below 8 leads to lower removal efficiency. To balance power input and removal efficiency, current should be applied at or above 30 A m^{-2} with an HRT in the middle of the range tested (i.e., 5–8 h).

3.2. Urine pretreatment: urea hydrolysis and salts precipitation

Total Kjeldahl nitrogen was lower in our sampled urine composite than expected from previous reports (Kuntke et al., 2013; Udert et al., 2006), at an average of 5.3 between the two composites, and thus is lower than the synthetic solution. Urea hydrolysis in real urine occurred rapidly upon urease addition, and initiated precipitation of phosphate, magnesium and calcium. Major components of each batch before and after hydrolysis are listed in Table 1. Upon urease addition, on average, pH increased from 6.6 to 9.3, conductivity increased from 14 to $36 \mu\text{S cm}^{-1}$, and approximately 91% of TKN was released (via hydrolysis) as TAN.

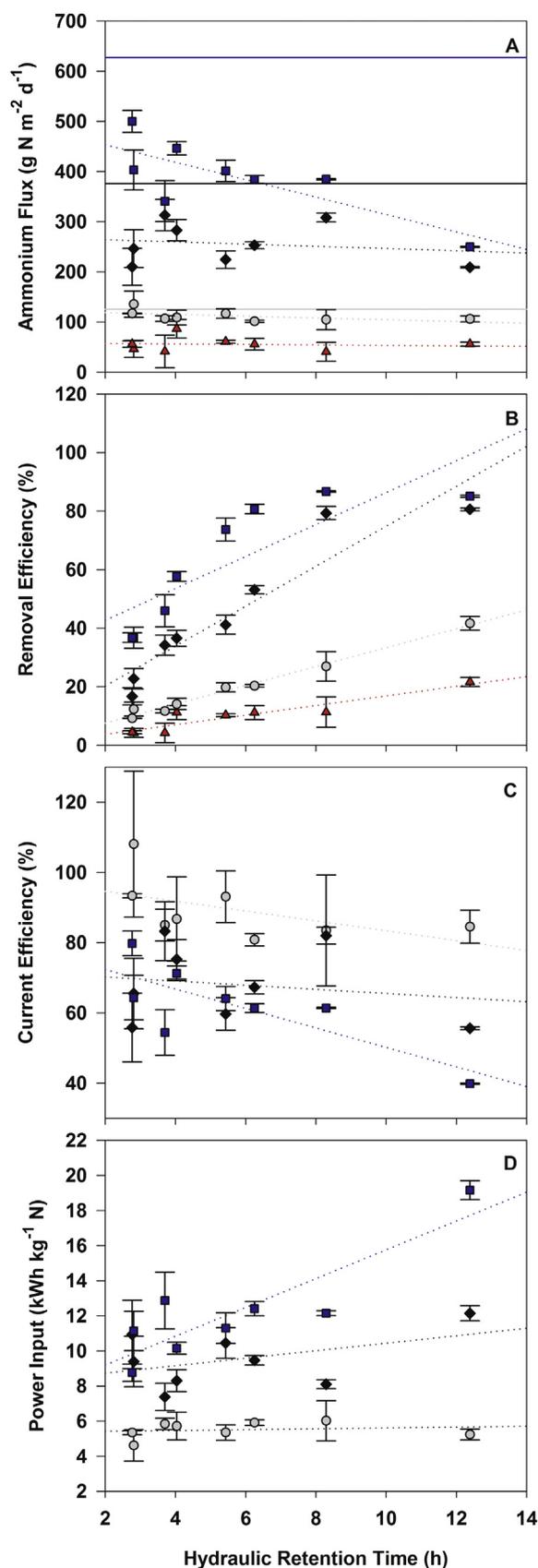


Fig. 2. Effect of hydraulic retention time on ammonium ion flux (A), ammonia removal efficiency (B), current efficiency of ammonium ion (C), and electrical cost (D) for runs at open circuit (red triangles) and applied currents of 10 (gray circles), 30 (black diamonds), and 50 (blue squares) $A m^{-2}$. Averages of three samples over steady state are

Precipitates began to form immediately upon hydrolysis and settled to the bottom of the reaction vessel. Phosphate, magnesium, and calcium precipitated and were removed from solution at 46–54%, 97–98%, and 48–56%, respectively. Neither sodium nor potassium were removed from solution, thus these cations are expected to be major competitors against ammonium ions for electrochemical transport across the cation exchange membrane.

3.3. EC performance for ammonium ($NH_4^+ - N$) extraction: real urine

Performance of the electrochemical cell over the course of the experiment was stable for System I, but declined steadily for System II as ammonia stripping was introduced to the influent headspace. Fig. 4 shows key performance parameters under open circuit (day 1) and under an applied current density of $40 A m^{-2}$ (day 2–9 for System II; and day 3–10 for System I). $50 A m^{-2}$ was applied briefly on day 2 for System I. System I maintained an average nitrogen flux of $275 \pm 5 g N m^{-2} d^{-1}$ (9% of this was from diffusion based on the OC run), while System II reached nearly the same level ($235 g N m^{-2} d^{-1}$) on day 2, but dropped steadily to $83 g N m^{-2} d^{-1}$ by day 9 (Fig. 4A). Likewise, System I maintained stable power input, ammonia removal efficiency, and CE while System II performed similarly at day 2, but thereafter deviated from the performance of System I (Fig. 4B–D, values provided in Table 2). On day 3 of the system II run, the anolyte flow rate was increased to reach $0.5 L d^{-1}$ (daily measurements indicated flow rate was low), which is the likely cause for the brief increase in flux and CE values at day 4 (Fig. 4A,C).

In system I the air pump failed on day 6 but was cleaned and working again by day 7. Between days 3 and 6 the vacuum pump responsible for stripping the catholyte in System II failed, which is the likely cause for the rise in TAN levels in the catholyte from day 3–6 (Fig. S2B). The pump was replaced on day 6 and stripping resumed; evidenced by the drop in catholyte TAN. The vacuum pump stripping the anode influent feed bottle was also replaced at this time with a recently cleaned pump. It was after this pump change that influent TAN concentrations began to drop steadily in system II, suggesting that both pumps were performing poorly over the first half of the experiment.

The decline in System II performance followed a decrease in the anode influent TAN concentration from day 4 through 8, due to ammonia stripping from the headspace (Fig. S2B). Without headspace stripping, System I still experienced an initial loss of TAN between 17 and 19% from the influent by day 3 but anode influent TAN concentration was stable for the remainder of the run (Fig. S2A). A slight drop in anode influent pH was observed in both systems, concurrent with the drop in influent TAN. In the case of System I, this TAN decrease was only seen in the first few days where the pH dropped from 9.4 to 9.2, then remained stable around 9.2 for the remainder of the run. In system II, the initial anode feed pH was 9.2, dropping to 9.1 over the first 5 days, then dropping steadily over the remainder of the run (concurrent with decreasing TAN) to a final pH of 8.5.

System II did succeed in maximizing total nitrogen recovery reaching a total of 77% (by the end of the run) compared with $57 \pm 0.5\%$ for System I (Table 2). As influent TAN dropped from 4.1 to

reported with standard deviation. Reference lines indicate maximum migrational flux, color coded for each applied current. Regression analysis was performed for each series. R^2 values are as follows for each plot (A–D) in the order OC (A and B only), 10, 30, $50 A m^{-2}$: (A): 0.01, 0.28, 0.03, 0.61; (B) 0.86, 0.99, 0.88, 0.71; (C) 0.28, 0.03, 0.6; (D) 0.03, 0.19, 0.76. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

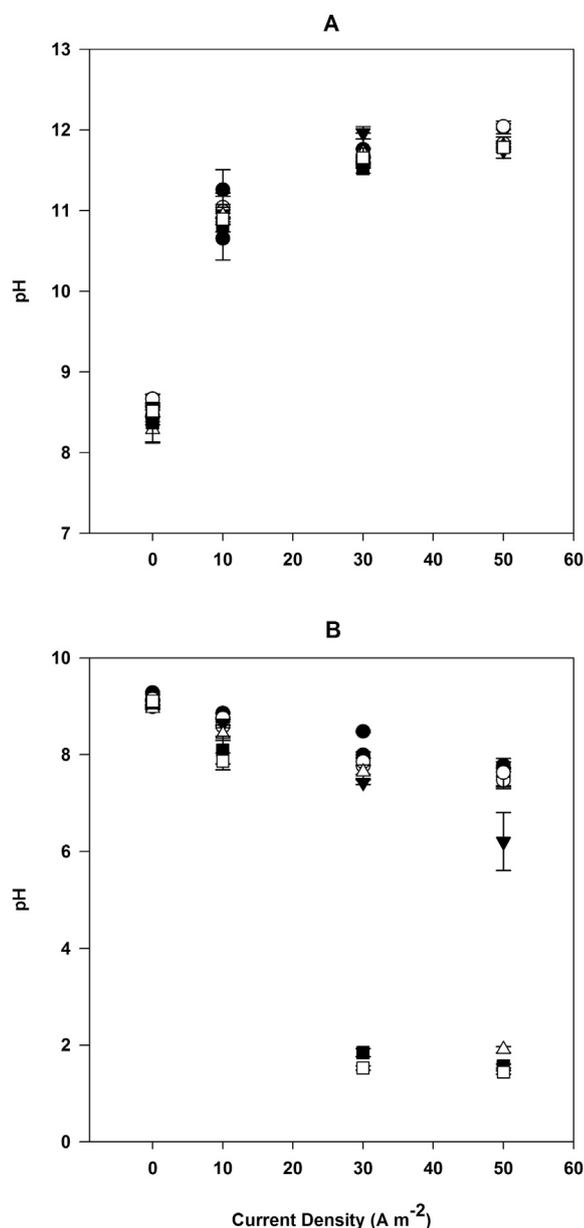


Fig. 3. Cathode (A) and anode (B) pH for each EC run with synthetic urine. HRTs (h): 2.8 (closed circles), 4 (open circles), 5.4 (closed triangles), 6.3 (open triangles), 8.3 (closed squares), 12.4 (open squares).

1.6 g L⁻¹ from day 6–9, power input rose sharply from 16 to 41 kWh kg N⁻¹ (Fig. 4D), and current efficiency for ammonia dropped from 47 to 16% (Fig. 4C). Decreasing influent TAN had the least effect on ammonia removal efficiency, as it dropped from 76 to 65%.

Current efficiencies for other major ion species in the urine were calculated for runs with real urine. CEs were stable in System I, with ammonium transport accounting for the majority of charge balance, followed by proton/hydroxyl ion, sodium, then potassium, with 55, 20, 16, and 8% efficiencies, respectively (Fig. 5A). CEs in System II started out the same as in System I, but as anode influent TAN decreased, the CE of ammonium decreased to 15% with a concomitant increase in the CE of protons/hydroxyl ion to 63% (Fig. 5B). This is likely the result of a drop in both the pH (Table 2) and TAN concentration (Fig. S2B) in the anode effluent. Calcium CE was less than 0.1% in both systems, and no transport of magnesium was detected. Some hydroxyl leakage can occur even across a CEM (Rozendal et al., 2008) but could not be differentiated from proton flux here. The EC was disassembled after each run with real urine to inspect the membrane and electrodes. Some white precipitate was observed in the cathode compartment and against the cathode facing side of the cation exchange membrane. Anode, cathode, and cell potentials were stable over the 9–10 day run tested here (Supplementary information, Fig. S1).

3.4. Ammonia recovery by direct stripping from urine

Direct stripping of the hydrolyzed urine achieved high total nitrogen recovery at high HRT. Total nitrogen recovery by stripping increased from 3% at 1 h to 83% after 77 h (Fig. 6) with corresponding removal capacities of 7.6 to 0.9 g N L⁻¹ d⁻¹, and recovery capacities of 4.1 to 0.6 g N L⁻¹ d⁻¹. The disparity between removal and absorption rates at any time point indicates nitrogen was lost from the system. The disparity observed in the first hour corresponds to an absorption efficiency of only 49%. An average absorption efficiency of 95 ± 5% was observed for the remainder of the experiment, indicating these losses were limited to the first few hours. Equilibration of NH₃ within the headspace may account for this loss, and accounts for only 3.4% of the total nitrogen in the system. System III cannot be directly compared against systems I since it was run as a batch system. To roughly compare the performance of the EC to direct stripping in terms of ammonia removal rates, removal capacities are used to compare the volumetric rate of ammonia removal in each system at similar HRT, since HRT has a substantial effect on removal rates in each system. The removal capacity for system III, calculated from the 6.2 h time point (reference line, Fig. 6) was 1.6 g N L⁻¹ d⁻¹, while that for system I

Table 1
Chemical composition of urine batches A and B before and after urease treatment.

Component	Synthetic urine	Urine batch A		Urine batch B	
		Before hydrolysis	After hydrolysis	Before hydrolysis	After hydrolysis
TKN (g L ⁻¹)	8	5.5	5.8	5	5.7
TAN (g L ⁻¹)	8	0.3	4.8	0.2	4.9
PO ₄ ³⁻ (g L ⁻¹)	0.1	0.5	0.2	0.6	0.3
Mg ²⁺ (mg L ⁻¹)	0	59.8	1.5	59.2	1.5
Ca ²⁺ (mg L ⁻¹)	0	105.4	55.2	107.9	47.5
K ⁺ (g L ⁻¹)	1.9	1.9	1.9	1.9	1.9
Na ⁺ (g L ⁻¹)	2.4	2.4	2.4	2.1	2.0
Cl ⁻ (g L ⁻¹)	4.5	3.2	2.9	3.2	2.9
SO ₄ ²⁻ (g L ⁻¹)	1.1	0.7	0.7	0.8	0.8
pH	9.1	6.6	9.4	6.6	9.2
Conductivity (mS cm ⁻¹)	54	15.5	35.7	12.7	37.8
COD (g L ⁻¹)	0	6.9	6.5	7.0	7.0

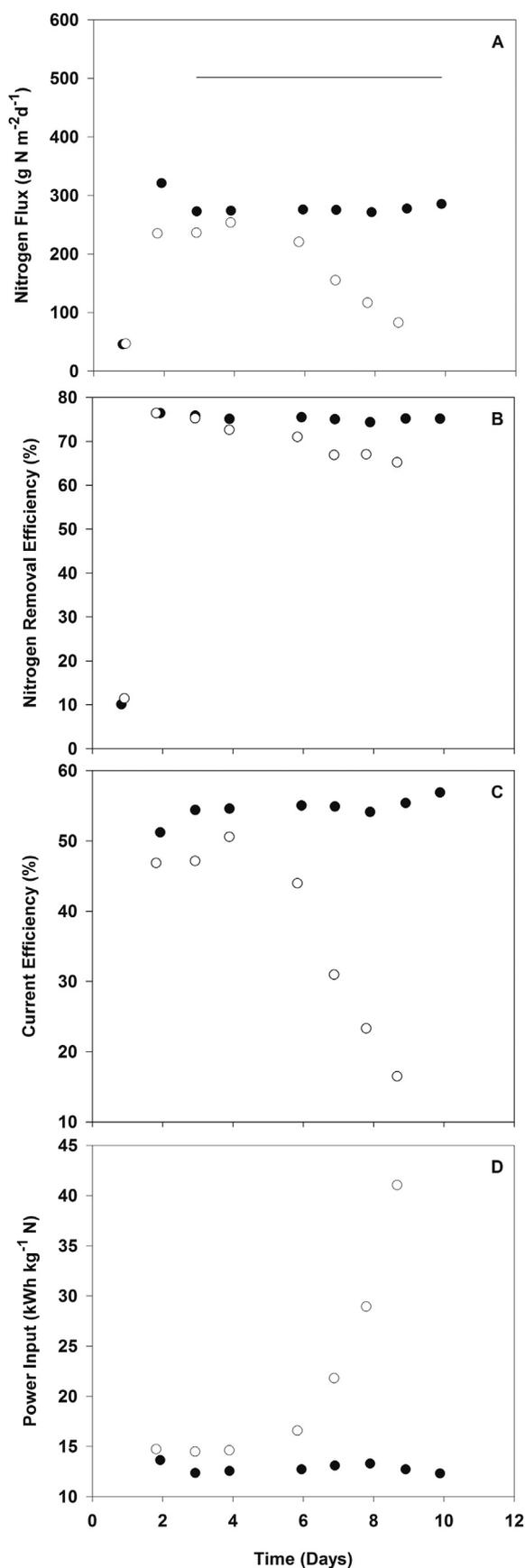


Fig. 4. Performance of EC System I (closed circles) and System II (open circles) over the course of each run with real urine. Reactors were operated for one day under open

was $14.5 \pm 0.2 \text{ g N L}^{-1} \text{ d}^{-1}$. Direct stripping displayed a lower removal capacity, by nearly 10 fold, e.g., a longer HRT is required to reach the same level of ammonia removal as the EC.

3.5. Stripping efficiency, absorption efficiency and nitrogen balance

Nitrogen recovery efficiencies, as calculated, reflect the stripping efficiency from the catholyte and were similar for both Systems I and II (Table 2). Vacuum pump failure occurred in both System II and III runs, and pumps had to be removed and cleaned in each case, resulting in at least two days of pump downtime. This first failure resulted in an increase in the TAN concentration in the catholyte to 2.9 g L^{-1} on day 6 in System I (Fig. S2A), however, the initial steady state TAN concentration resumed after the pump was reinstalled. Excluding periods when stripping or headspace evacuation was off, System I had an average recovery efficiency of $75 \pm 0.6\%$. System II had an initial recovery efficiency of 58%, which increased to an average of $76 \pm 1.4\%$ over the last three days (following a vacuum pump downtime).

Absorption efficiency in System I was initially 95% but decreased to 60% by the end of the run. System II exhibited an increase in the catholyte effluent concentration from day 2 through 4, at which point gas flow through the absorption unit had noticeably slowed. The pump was replaced on day 6 and cathode effluent subsequently dropped sharply. Absorption efficiencies for System II thus reached 94% on day 2, and 96% on day 9, but dropped in between these two points, likely due to pump malfunction. Absorption efficiencies remained $>90\%$ after 5 h for System III. The nitrogen balance at the beginning of the run for System I was 97%, but dropped to 79% by the end of the run. The overall, average, nitrogen balance was 80% for System II and 100% for System III.

4. Discussion

4.1. Optimizing performance of the EC system

Optimizing the EC system requires a compromise between ammonia removal efficiency (treatment) and power input for this recovery (cost). Higher removal efficiency indicates lower residual nitrogen in the effluent i.e. a more complete treatment. However, achieving low residuals in this system requires a proportionally higher applied current and/or a longer HRT, both of which lead to a lower CE, which in turn leads to an increase in the cost of nitrogen removal (kWh kg N^{-1}) from the system. Increasing the applied current, or increasing the HRT both increased the proton concentration in the anode by increasing the proton production rate or accumulation, respectively. In the EC system, HRT and current density can be adjusted to control the anode pH in order to optimize the reactor performance. Although total recovery of nitrogen was increased by the addition of influent headspace stripping, the decline in performance of the EC on every other level in System II makes this additional recovery more costly. More importantly, System II served to demonstrate the strong effect influent TAN concentration has on practically every measurement of EC performance.

The high loss of TAN from the influent vessel during the first three days of the system I run was not expected and cannot be explained from these experiments. The high pH and high ionic strength of the hydrolyzed urine may lead to some volatilization of

circuit. Beginning on day 2 a current density of 40 A m^{-2} (System II) or 50 A m^{-2} (System I) was applied, and by day 3 both reactors were operating at 40 A m^{-2} . The solid line on graph A indicates the maximum theoretical ammonium flux for either system.

Table 2
Comparison of performance and operational parameters across the EC systems tested here and two bioelectrochemical systems treating urine.

Parameters	Synthetic urine (EC only)		EC system (I) ^a	EC system (II) ^b	MEC ^c	MFC ^d
Applied current density (A/m ²) ^f	30	50	40	40	14.64 ± 1.65	0.5
Influent TAN (g N L ⁻¹)	6.5	6.5	4.8 ± 0.0	5.1, 1.7	0.7	4.1
Influent pH	9.1	9.1	9.2 ± 0.1	9.2, 8.5	9.1	8.9
Anode effluent TAN (g L ⁻¹)	3 ± 0.1	1.3 ± 0.1	1.2 ± 0.03	1.1, 0.6	n.r.	n.a.
Nitrogen flux (g N m ⁻² d ⁻¹)	253 ± 7	384 ± 7.7	275 ± 4.57	235, 82.7	175	3.3
Current efficiency (%)	67 ± 2	61.3 ± 1.2	55 ± 0.9	47, 16	95 ^e	31
Nitrogen removal efficiency (%)	53 ± 1.0	80.7 ± 1.6	75 ± 0.5	76, 65	33.9 ± 0.6	n.r.
N recovery efficiency (%)	n.a.	n.a.	76 ± 0.6	58, 76	n.r.	n.r.
Total nitrogen recovery (%)	n.a.	n.a.	57 ± 0.5	53, 77	n.a.	0.6 ^e
Power input (kwh kg N ⁻¹)	9.5 ± 0.3	12.4 ± 0.4	12.7 ± 0.37	14.7, 41.0	2 ^e	n.a.
Anode pH	7.6 ± 0.1	1.9 ± 0.1	2.5 ± 0.12	2.0, 1.5	7.5 ± 0.3	8.9
Cathode pH	11.7 ± 0	11.8 ± 0.0	10.2 ± 0.2	10.6, 10.3	9.7 ± 0.1	n.r.
Anode HRT (hour)	6.2	6.2	6.0 ± 0.09	6.2 ± 0.5	1	0.015
Cathode HRT (hour)	0.7	0.7	10.5 ± 0.49	10.7 ± 0.9	6	air cathode
Cell potential (V)	3.3	4.0	3.7 ± 0.1	3.6 ± 0.1	1.0	0.5

n.a. indicates not applicable, n.r. not reported.

^a Average over day 3–10, excluding period of pump failure.

^b Values given for day 2 (beginning) and day 9 (end).

^c From Kuntke et al. (2014) an MEC treating diluted urine with catholyte NH₃ stripping, results from experiment D.

^d From Kuntke et al. (2012) an MFC with air cathode and NH₃ stripping.

^e Calculated values, see section supplementary material.

^f Current densities in BES studies are produced, not applied.

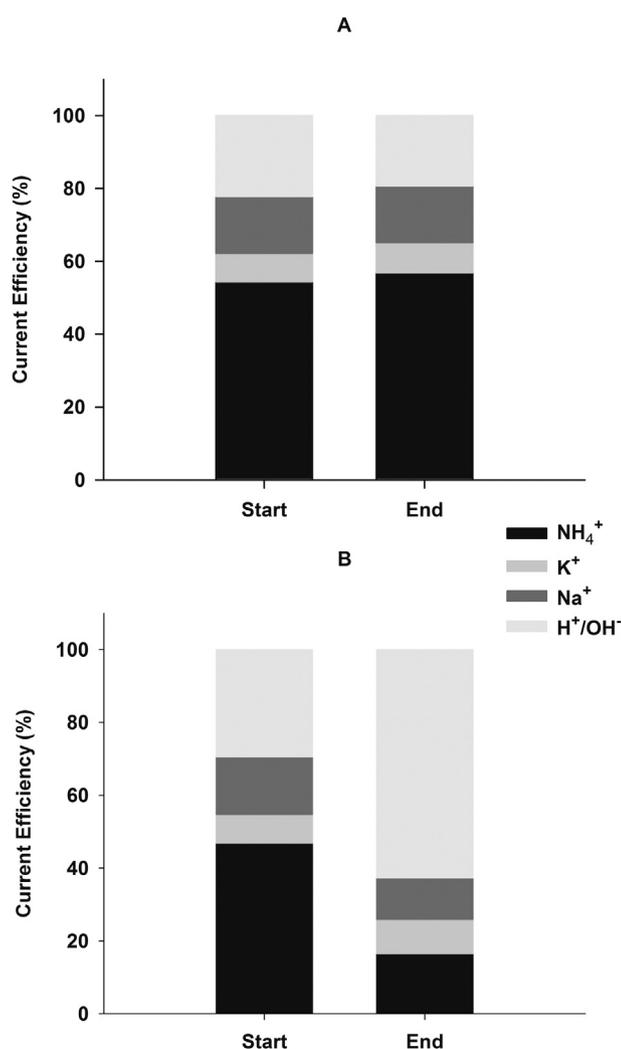


Fig. 5. Relative proportion of major cations transported across the CEM in Systems I (A), and II (B) at the start and end of each run.

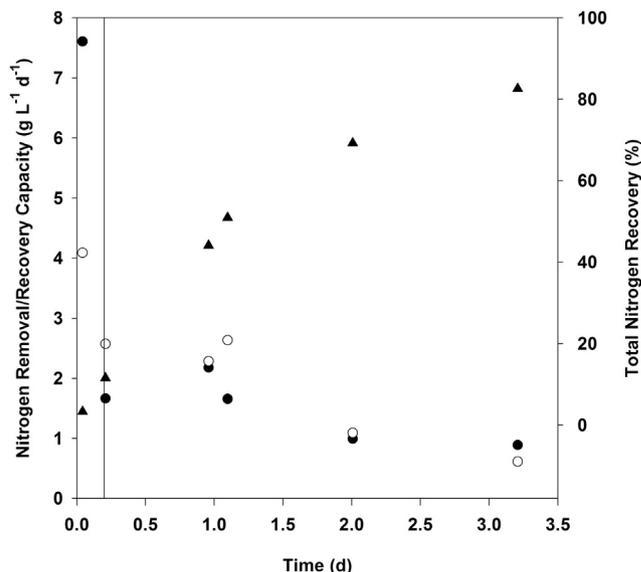


Fig. 6. Nitrogen removal capacity (closed circles), nitrogen recovery capacity (open circles), and total nitrogen recovery (closed triangles) from direct stripping (System III). Solid reference line marks a 6.2 h hydraulic retention time for comparison with Systems I and II.

ammonia, but equilibrium calculations cannot account for the observed 17–20% loss of TAN. Measurements of ammonia volatilization from stored urine (Udert et al., 2006) suggest the actual losses would even be lower than those calculated using Henry's Law due to slow mass transfer rates. Biological oxidation via microbial growth in the feed compartment could lead to ammonia loss (nitrification), however this would likely have been seen in both system I and II, and it such losses were not seen in the first few days of system II (no initial drop in TAN for system II, see supplementary material, Fig. S2).

The hydrolysis step succeeded in removing much of the phosphate, magnesium, and calcium ions from solution although magnesium was likely limiting to this removal. Precipitate composition was not measured here, but if we assume all Mg²⁺ removal is due to precipitation of struvite and/or potassium struvite, phosphate

removal cannot be fully accounted for only by struvite precipitation. In both urine batches A and B hydrolysis experiments, phosphate was removed at a molar ratio of 1.2:1 ($\text{PO}_4^{2-} : \text{Mg}_2^+$), where a 1:1 ratio would be expected for struvite formation. Enough calcium removal occurred to account for the formation of HAP from the remaining phosphate, leaving some additional calcium remaining. The last of this calcium may have precipitated as calcite. Some white precipitate was observed in the cathode compartment at the end of the experiment. Although very little (<0.1% of charge transfer) calcium transfer was detected, this may have been sufficient to cause precipitation over the course of the run. Scale formation in practice is undesirable, and should be further investigated.

Further optimization of the stripping and absorption system is necessary to improve this technology. The malfunctioning of the vacuum pumps used here limited the analysis of ammonia losses, especially during the system II run. Although the data following the replacement of these pumps suggests that the addition of head-space vacuuming lead to heavy desorption of the ammonia from the influent feed, the rate and extent of this TAN loss was higher than expected given the high solubility of ammonia. Further experiments to investigate ammonia desorption from urine are necessary. Alternative stripping configurations could further reduce the electrical cost of this technology. For example, the hydrogen gas produced at the cathode could be used to strip the ammonia from the gas via passive means, eliminating the need for energy intensive air pumps.

The EC driven ammonia extraction system performed somewhat better here than first demonstrated for application to digestate wastewater (Desloover et al., 2012). Ammonia flux, current efficiency, and removal efficiency from urine treatment were $275 \text{ g TAN m}^{-2} \text{ d}^{-1}$ 55% and 75% compared to $94 \text{ m}^{-2} \text{ d}^{-1}$, 25%, and 65% from digestate wastewater, respectively. This is likely due to the higher applied currents used here (40 vs. 30 A m^{-2} previously) and higher TAN content of the influent (4.8 g L^{-1} for urine vs 2.1 g L^{-1} for swine wastewater). Additionally, the higher K^+ concentration in swine wastewater ($5.1 \text{ vs } 1.9 \text{ g L}^{-1}$ in urine) contributed to a lower current efficiency for ammonium. The result is a lower electrical input for ammonia recovery from urine at $13 \text{ kWh kg}^{-1} \text{ N}$, vs 26 for the wastewater digestate treatment, even at higher applied current.

The potentials used here to drive water oxidation are also high enough to oxidize chloride ions (with formation of chlorine gas) or ammonia directly. Formation of chlorine is likely minimal due to the chosen electrode; Iron coated titanium has been demonstrated to have low activity towards chloride (Bagastyo et al., 2011). Direct oxidation of ammonia cannot be assessed here since it was not measured, however the nitrogen balance did reach 95% (based on absorption column measurements) in system I, suggesting oxidation of ammonia at the anode did not play a major role in losses here.

4.2. Comparison of EC systems with BES for ammonia recovery from urine

Comparing ammonia recovery from urine via the EC systems described in this study versus recovery using bioelectrochemical systems (BESs) is useful because of the increasing interest in the application of BES generally for treatment of various wastewaters (Pant et al., 2010), and specifically for source separated urine (Ledezma et al., 2015). Such a comparison was recently examined for systems treating anaerobic digestate (Gildemyn et al., 2015). Key operational parameters and performance measurements for EC systems investigated here are compared against data from recent studies of two different BESs treating urine in Table 2. The

comparison is somewhat hindered because of differences in feed composition and reactor configurations. For the MFC (Kuntke et al., 2012) and EC (this study) systems, undiluted urine with a TAN of $\sim 4\text{--}5 \text{ g N L}^{-1}$ was used as a feedstock; however, the MEC system (Kuntke et al., 2014) used 5-fold diluted urine (0.7 g TAN/L) as feedstock. Both anode and cathode chambers in the MEC used a chambered flow through design, which is different than the design used here. Further, the MFC system utilized an air cathode in contrast to the liquid cathode utilized by the MEC and EC (this study).

With respect to nitrogen flux the EC system performed better than both the MEC and MFC systems at high influent TAN concentrations. Nitrogen flux in System I was $275 \pm 4.57 \text{ g N m}^{-2} \text{ d}^{-1}$ compared with 175 in the MEC and 3.3 in the MFC (Table 2). However, as the anode influent TAN dropped in the EC (System II) flux dropped to $82.7 \text{ g N m}^{-2} \text{ d}^{-1}$, dropping below that of the MEC. The lower performance in the EC compared to MEC at now comparable influent TAN levels may be due to an increased relative flux of protons in the EC due to the low anodic pH (1.5) compared to that of the MEC (pH 7.5). Nitrogen removal efficiencies in the EC were more than double that of the MEC, even as influent TAN concentration dropped to 1.7 g TAN L^{-1} . Ammonia removal efficiency could not be calculated for the MFC, but the total recovery (includes removal efficiency and absorption efficiency) was only 0.6%, nearly 10-fold lower than that of the EC system. Current efficiency for ammonia was highest in the MEC system at 95% compared to 55% in the EC (System I), and 33% in the MFC system. The higher CE for the MEC was likely caused by a smaller current and higher residual N concentration in the anode, leading to a higher relative contribution of diffusion to overall transport. Of additional note here is the difference in the anode pH, which remained above 7 in the BESs, but dropped to near 2 in the EC systems where higher currents were applied.

The advantage of the EC over the two BES considered here is largely due to the higher applied currents in the EC systems, since both flux and removal efficiency are directly limited by the current. In the BES current production is limited by the microbial activity at the anode, which is in turn ultimately limited by the available COD in the urine. Additionally, any biological process will be sensitive to environmental factors such as pH, chemical toxicity (e.g. ammonia), and carbon loading. As demonstrated with the EC system, anode pH can drop severely, dependent on the current, TAN concentration, and buffering capacity of the solution. In both the MEC and MFC, pH remained near neutral, but fluctuating influent concentrations and/or increased current production could lead to unstable anodic pH. When undiluted urine is used as influent, ammonia toxicity may inhibit the microbial process; this may explain the low current densities observed in the MFC. Dilution of the urine also means a lower COD, which could limit current production. The BES approach has the advantage of producing (MFC) or consuming less (MEC) power, which may translate to a lower recovery cost. However, the strictly electrochemical approach has the advantage of greater stability, predictability, and flexibility in terms of controlling the reactor. Moreover a considerable hydrogen flux accompanies the NH_3 , enabling recovery of energy via this hydrogen to a level of $3.8 \text{ kWh per kg NH}_3$. Waste oxygen generated at the anode can further be used to degrade the COD of the urine.

The EC may have an advantage over the BES since influent feed concentration and flow (urine collection throughout the day) can vary greatly (Rose et al., 2015). While COD removal may be seen as a benefit to the BES system, this in fact limits the system with respect to obtainable current density (current production is dependent on microbial consumption of COD) and thus flux. Based on our data, it also appears the electrochemical system is capable of a higher overall ammonia recovery, due mainly to the ability to produce

higher current densities which deliver greater nitrogen flux.

4.3. Potential to reduce wastewater treatment costs

We have demonstrated here that an electrochemical system can be used successfully to recover ammonia from concentrated urine with high efficiency and moderate cost. We envision application of this technology in a decentralized treatment scenario whereby highly pure ammonia and hydrogen gas are recovered as valuable products against the cost of treatment. The highest ammonia flux achieved here was with the synthetic urine, at $500 \text{ g N m}^{-2} \text{ d}^{-1}$. By comparison the highest flux observed with real urine was only $276 \text{ g N m}^{-2} \text{ d}^{-1}$. The higher flux observed with the synthetic urine is likely due to the higher TAN concentration of the synthetic feed (near 7 g TAN L^{-1}), and the lower HRT (2.8 h in this particular run, vs 6 h HRT for real urine runs). Despite these differences, removal efficiencies were comparable for the synthetic and real urine, as we saw nearly 80% ammonia removal efficiency across the EC for both feeds. Total nitrogen recovery from the real urine was 57%, reflecting losses due to the efficiency of the stripping/absorption unit. Discharge of anode and cathode effluent to the sewer system with these removal rates would still substantially reduce the nutrient load to wastewater treatment plants and thus reduce costs at these facilities. Considering that urine accounts for about 75% of the nitrogen input at a WWTP, this technology could reduce the nitrogen load to the plant by 43%. The cost of the recovery through the EC ($\sim 13 \text{ kWh kg N}^{-1}$) is higher than the cost of ammonia production via Haber–Bosch ($\sim 10 \text{ kWh kg N}^{-1}$), but has the additional benefits of decreasing downstream wastewater treatment costs lowering emissions along the sewer line, and production of hydrogen gas worth $3.8 \text{ kWh kg N}^{-1}$. Furthermore, the alkaline solution (cathode effluent) could aid in optimization of salt precipitation during the pretreatment, or holding stage. If additional benefits such as decreased treatment needs are considered, recovery of ammonia from wastewater could provide an attractive alternative source of ammonia nitrogen. The cost of EC recovery with and without hydrogen recovery are presented with treatment costs of other leading technologies in Table 3.

One of the greatest advantage of electrochemical recovery over direct stripping or precipitation of ammonia from complex wastes, such as urine, is the high purity of the final product resulting from selective removal and absorption. Zlatkis and Liebich (1971) identified 75 volatile constituents in the range of 10 ng to 100ug per

urine sample. These compounds are not discussed or considered, as far as we are aware, in any investigations of ammonia stripping from urine. This is something that should be considered, and could reduce the purity of the final ammonium sulfate product. Thus, while recovered ammonium sulfate could serve as a fertilizer, a more lucrative application might be to use it to produce higher value products such as feed and food, or for industrial applications for synthesis of nitrogen polymers, such as DeNOx (Matassa et al., 2015).

Further studies are necessary to assess the integrity of the electrodes and cation exchange membrane over long-term treatment. In this study, no corrosion was observed, but some precipitation was observed in the cathode compartment. Membrane integrity could be a primary limitation to this technology. It is also important to note that since this system relies on electricity, the primary energy source of the electricity used will greatly impact the true energy cost of the system (based on fuel conversion efficiencies). This may be seen as a disadvantage in a fossil fuel economy, but could be an advantage as alternative and sustainable electricity sources become available.

5. Conclusions

- EC extraction of ammonia from synthetic urine (post hydrolysis) was evaluated under a range of HRT and applied currents, and performance was similar with real urine
- Headspace stripping was able to increase overall ammonia recovery, but the resulting decreases in influent TAN concentrations led to poorer EC performance in terms of ammonia removal and current efficiencies, which dropped from 76 to 65%, and from 47 to 16%, respectively.
- Direct stripping could attain high ammonia recovery (80%), but had a lower removal capacity ($1.6 \text{ g N L}^{-1} \text{ d}^{-1}$) compared to EC system ($14.5 \text{ g N L}^{-1} \text{ d}^{-1}$).
- Higher ammonia flux and removal efficiencies were achieved through the EC approach as compared to the BES approach due largely to higher current densities
- Electrochemical extraction appears to be a promising technology for ammonia recovery from complex wastewaters containing high concentrations of ammonia and should be further investigated for application in treatment of source separated urine and anaerobic digestates of various animal manures.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2015.09.041>.

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Table 3

Comparing energetic costs of established technologies for nitrogen treatment and production.

Treatment method	MJ kg ⁻¹ N	kWh kg ⁻¹ N
Nitrification/denitrification in WWTP ^a	14	4
Struvite precipitation for nitrogen removal ^b	81	23
Stripping ^c	32	8.9
Electrochemical extraction ^d	47	13
Electrochemical extraction with hydrogen recovery ^e	31	9
Ammonia production by Haber–Bosch ^f	37	10

^a Includes electrical costs (aeration), WWTP = wastewater treatment plant, see Maurer et al. (2003).

^b Includes chemical costs (magnesium oxide and phosphoric acid), see Maurer et al. (2003).

^c Includes chemical costs (calcium oxide and sulfuric acid) and electrical costs (aeration), see Maurer et al. (2003).

^d Includes average electrical cost of ammonium transfer through system I of this study, (catholyte stripping only) and chemical cost of sulfuric acid included assuming $1.1 \text{ MJ kg}^{-1} \text{ N}$.

^e Savings from recovery of hydrogen deducted from cost of electrochemical extraction, assuming conversion factor of $33 \text{ kWh kg}^{-1} \text{ H}_2$.

^f Includes fuel costs (supplied by natural gas), see Maurer et al. (2003).

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