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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 ± 8 g N m^{-2} d^{-1} with a 61 ± 1% current efficiency at an energy input of 12 kWh kg^{-1} N removed. EC processing of real urine displayed similar performance, with an average ammonium flux of 275 ± 5 g N m^{-2} d^{-1} sustained over 10 days with 55 ± 1% current efficiency for ammonia and at an energy input of 13 kWh kg^{-1} N removed. With the incorporation of an ammonia stripping and absorption unit into the real urine system, 57 ± 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 kWh kg^{-1} N. Considering also that the hydrogen generated is worth 4.3 kWh kg^{-1} N, the net electrical input for extraction becomes approximately 8 kWh kg^{-1} 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.

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 kWh kg^{-1} 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 ($MgNH_4PO_4 \cdot 6H_2O$) 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 $(NH_4)_2SO_4$ 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).

$$NH_2(CO)NH_2 + 2H_2O \rightarrow 2NH_3 + H_2CO_3 \quad (1)$$

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, $MgNH_4PO_4 \cdot 6H_2O$; hydroxyapatite $(Ca_5(PO_4)_3(OH)$; and calcite, $CaCO_3$)) in a urine collection system (Udert et al., 2003b). Synthetic urine contained (g L^{-1}): $(NH_4)_2CO_3$ (27.5), NaCl (4.72), KCl (3.6), $Na_2SO_4{-}10H_2O$ (3.9), KH_2PO_4 (70 mg L^{-1}), and K_2HPO_4 (90 mg L^{-1}). This assumes 97% $P-PO_4{}^{3-}$ 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. Lois, 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 × 8 × 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 m^2 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