Electrochemical Stripping to Recover Nitrogen from Urine

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Abstract
Electrochemical stripping, a novel extension of electrodialysis, was used to recover nitrogen from source-separated urine. Urine has high nitrogen concentrations, making it an ideal waste stream for nitrogen recovery. A three-chamber, two-membrane cell was used to measure efficiencies and barriers to nitrogen migration. In preliminary batch studies, half of the influent nitrogen was recovered as ammonium sulphate, which can be used as a fertilizer. Obstacles to nitrogen migration include the production of chloramines, which can be avoided by controlling electrode materials and operating voltage. This proof-of-concept study makes the way for more detailed investigations that will lead to process optimization for maximal nitrogen recovery efficiency.

Keywords
nitrogen; source separation; urine; electrochemistry

INTRODUCTION

Conventionally, nitrogen is removed from wastewater via base addition and ammonia stripping or nitrification/denitrification (Siegrist, 1996). Electrochemistry has emerged as an attractive treatment option because of its scalability, flexibility, and on-site chemical production (Chen, 2004). Electrochemical cells have recently been identified as a potential method for removing nitrogen from concentrated wastewater and anaerobic digestate; they can also be used to recover nitrogen from source-separated urine (Desloover, Woldeyohannis, et al., 2012; Luther, Desloover, et al., 2015). Urine is a promising waste stream for nitrogen recovery because it comprises only 1% of wastewater volume but contains 80% of nitrogen present in wastewater (Larsen, Udert, et al., 2013).

Two research directions are being pursued for electrochemical nitrogen removal from urine: electrolysis and electrodialysis. Electrolysis technologies remove ammonium from urine by oxidizing it to N_2 or chloramines (Zöllig, Fritzsche, et al., 2015). In electrodialysis, ammonium is neither oxidized nor reduced; its migration across a cation exchange membrane is induced by the transport of electrons through an external circuit. This idea has been applied to urine by supplying electricity to separate nitrogen and phosphorus from micropollutants (Pronk, Biebow, et al., 2006).

Electrochemical stripping, a form of electrodialysis, improves upon conventional ammonia stripping in two ways: (1) pH increase without base addition and (2) internal NH_3 stripping without a tower. In this study, we investigated recovery in a three-chamber, two-membrane design comprised of anodic NH_4^+ migration, cathodic conversion to NH_3, and reconversion to NH_4^+ in an acid trap (Figure 1). At the anode, urine is fed into the cell and applied current powers water oxidation and subsequent separation of electrons and cations (like NH_4^+). Once separated, ammonium ions cross a cation exchange membrane and produce aqueous ammonia (NH_3) at the basic cathode. The catholyte is in contact with a gas permeable membrane through which gaseous ammonia diffuses. The transport of gaseous ammonia induces further ammonia volatilization in the cathode compartment. A dilute sulfuric acid solution on the other side of the gas membrane converts ammonia to ammonium (Tan et al., 2006). Compared to current electrodialysis technologies, electrochemical stripping is a novel extension focused on nitrogen recovery rather than removal, which can lead to the production of fertilizers.

Our specific objectives with respect to electrochemical stripping were: (i) to quantify nitrogen recovery and (ii) to characterize and overcome barriers to nitrogen migration between chambers.

MATERIALS & METHODS

In batch studies, nitrogen recovery efficiency is defined as the ratio of ammonium concentrations in the acid trap and influent anode chamber. Total ammonia nitrogen (TAN) is measured via ion chromatography at multiple time points in each of the three chambers. pH and temperature are also measured to differentiate between NH_3 and NH_4^+.

Cyclic voltammetry is an electrochemical technique useful for identifying predominant reactions. By varying voltage, peaks in current density emerge at voltages characteristic of certain reactions. Creating cyclic voltammograms for different influents allows for comparison of the reactions in each solution. Similar comparisons can be made between batch and continuous flow.

The methods used to identify and overcome barriers to nitrogen migration are unique for each of the three chambers and two membranes in the electrochemical stripping system. At the anode, the operating potential could theoretically also lead to chloride and ammonia oxidation.45 We measured the products of these reactions, HOCl and NO_3^-, to confirm predominant reactions. (DPD method and anion chromatography, respectively). Competitive migration across the cation exchange membrane was quantified by Coulombic efficiency, the proportion of electrons generated that are matched by the transport of a given ion. Measuring ammonium, sodium, potassium, and proton concentrations in both the cathode and anode allows for the calculation of a Coulombic efficiency for each ion. Proton concentration is calculated from pH measurements; the other cations are measured by cation chromatography. At the cathode, pH, temperature, and total ammonia nitrogen measurements were used to calculate aqueous NH_4^+ and NH_3 concentrations. NH_3 transport across the gas permeable membrane was characterized by comparing TAN and pH in the cathode and acid trap; flux and mass transfer coefficients will be compared to theoretical calculations based on stripping from NH_4Cl solutions (Hasanoğlu, Romero, et al., 2010). Finally, the acid trap's pH and TAN were monitored to measure the driving force for aqueous NH_3 diffusion and absorption.

RESULTS & DISCUSSION

A 24-hour batch experiment showed 50% recovery in the trap, 15% recovery in the cathode chamber, and 5% remaining in the anode chamber (Figure 2). A non-negligible mass of nitrogen (30%) was unaccounted for in the course of the experiment. Cyclic voltammograms from batch treatment of all three solutions (pure salt, synthetic, real urine) are shown in Figure 3. The peaks at approximately 1.3 V are characteristic of the expected oxidation of water at the anode; however, synthetic and real urine solutions exhibited an extra peak relative to ammonium sulfate at about 0.6 V. Given the unaccounted loss of nitrogen and the extra peak in the cyclic voltammograms for synthetic and real urine, chlorine oxidation was explored as a competing reaction to water oxidation. Preliminary results indicate that chloramines are produced during electrochemical stripping. Results from current experiments documenting this mass balance will be presented in the full paper. Process parameters like membrane and electrode materials, operating voltage, and flow rate, will also be adjusted to optimize nitrogen recovery efficiency.

CONCLUSION

In this study, the nitrogen recovery was examined in a three-chamber, two-membrane electrochemical stripping cell. The addition of passive membrane stripping can lead to higher efficiencies and nitrogen recovery rather than removal. Mass balances were used to track nitrogen migration and speciation in each chamber. Cyclic voltammetry was used to determine predominant reactions in the anode and cathode chambers. Preliminary results showed 50% recovery in the trap chamber and an unaccounted mass that is likely lost due to chloramine formation. In further studies we will elucidate barriers to nitrogen recovery and adjust operating parameters for optimal nitrogen recovery efficiency.

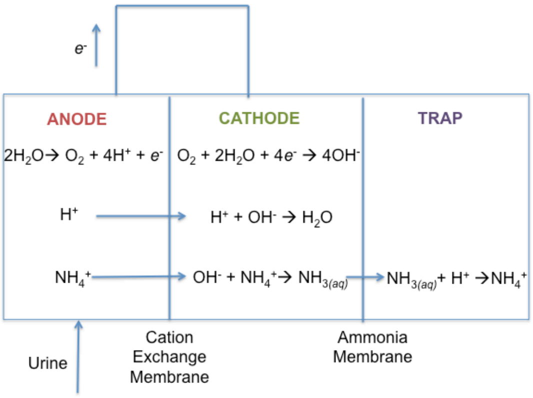

Figure 1. Schematic of electrochemical stripping process.

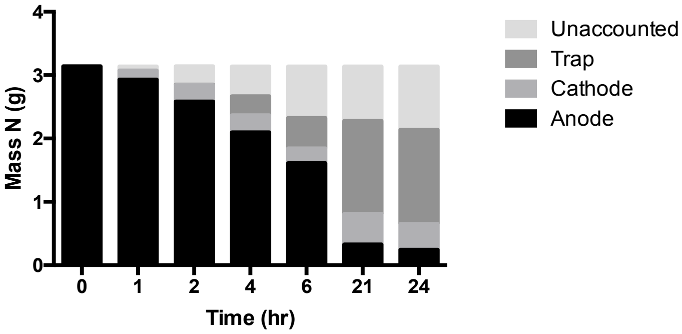

Figure 2. Mass balance for total ammonia nitrogen in three chambers of electrochemical stripping cell.

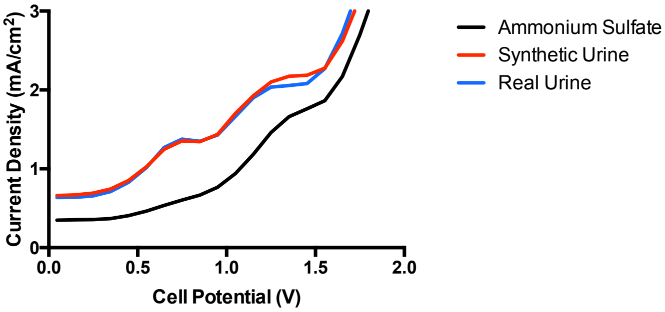

Figure 3. Cyclic voltammograms in varied influents with initial ammonium concentrations of 7000 mg N/L. Only oxidation curve is shown for each solution. Peak at 1.23 V characteristic of water oxidation.

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