ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

Evaluation of a Urea Bioelectrochemical System for Wastewater Treatment Processes

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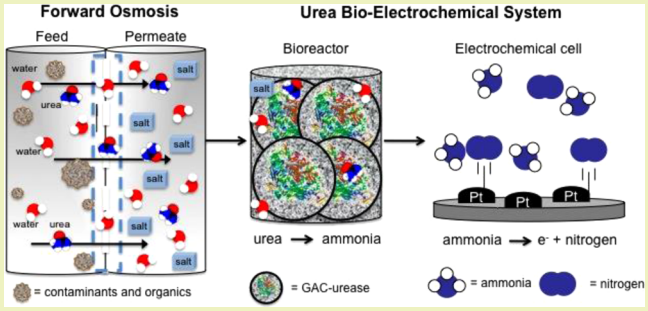
ABSTRACT: Due to the high cost of delivering supplies to space, the recovery of potable water from spacecraft wastewater is critical for life support of crewmembers in short- and long-term missions. It is estimated that in future long-term space missions, human wastes such as urine will contribute more than 50% of the total waste. Thus, we will demonstrate how unused components, such as urea, can be recovered and reused in wastewater recycling processes. In this system, a urea bioreactor (GAC-urease) converts urea to ammonia. Then, an electrochemical cell converts the ammonia to power. The combined system is referred to as the Urea Bioreactor Electrochemical (UBE) unit. The results of this research showed the feasibility of interfacing wastewater-recycling processes with bioelectrochemical systems to achieve water recycling while reusing useful resources. The UBE systems removed >80% of organic carbons and converted approximately 86% of the urea to ammonia. Therefore, the concept herein proposed has the potential to be used in water recycling applications with emphasis in contaminant recovery from wastewater for useful resources and energy.



KEYWORDS: *Resource recovery, Water reclamation, Urea degradation, Electrochemical cell, Bioreactor*

INTRODUCTION

The three sources for wastewater reclamation and reuse in short- and long-term space missions are humidity condensate, hygiene, and urine wastewater. It is estimated that in future manned long duration missions, human wastewater will contribute 54% (1918 g/crewmembers-d) of the total wastes per person in a daily basis. Urine is expected to contribute 1562 g/crewmembers-d, based in a diet of 59 g/crewmembers-d of solid and 1503 g/crewmembers-d of water.[1] Therefore, water recycling has been established as among one of the most important issues for future manned long-term (i.e., 120−400 day) space missions.[2] Undoubtedly, the high launch costs of fresh water to space and environmental health of crewmembers are major contributing factors for the research interest in the field of water reclamation and reuse. Because approximately 81.4% of human wastewater in space is urine, wastewater treatment systems for spacecraft must address urine wastewater recycling.

Recent investigations have evaluated the potential of integrating forward osmosis (FO) along with biological/electrochemical technology for the treatment of wastewater and electricity generation. Zhang et al. reported on the integration of a FO system into a microbial fuel cell for wastewater treatment and energy generation. This work demonstrated enhanced water flux with a power output of 4.74 W/m.[3−5]

This research is a proof-of-concept for the development of a Urea Bioreactor Electrochemical system (UBE) to be used with wastewater treatment systems to convert urea into ammonia and ammonia into power. UBE consists of a bioreactor and an electrochemical cell. In the bioreactor, the urea reacts with immobilized urease (GAC-urease) to form ammonia. In the electrochemical cell, the product of the enzymatic reaction is electrochemically oxidized at the interface of a platinized boron-doped diamond electrode to generate current (Figure 1). Urease (EC 3.5.1.5, urea amidohydrolase) is a nickel metalloenzyme that catalyzes the hydrolysis of urea to produce two moles of ammonia and carbonic acid (eq 1).[6,7] This research uses solutions from the FO/RO system at NASA ARC[8] because the wastewater components can be estimated. However, the results of this research can be applied to any wastewater recycling system to utilize either or both urea and/or ammonia in wastewater by converting them into power.

Received: October 22, 2013
Revised: February 14, 2014
Published: March 12, 2014

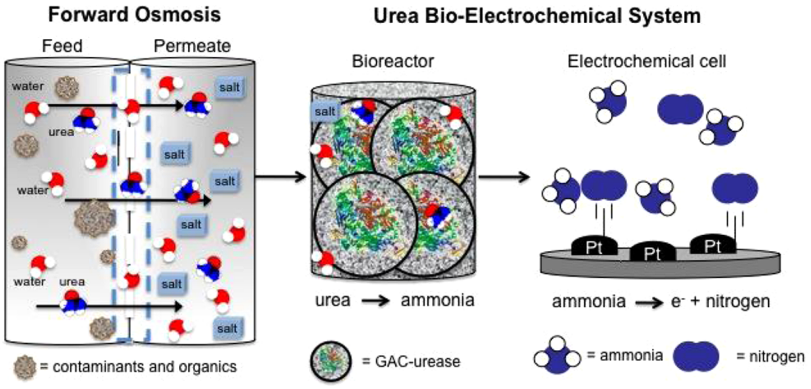


Figure 1. Schematic of the proposed FO–UBE system showing the two-step process for the recovery of urea from forward osmosis to energy and useful resources.

$$CO(NH_2)_2 + 2H_2O \xrightarrow{\text{Urease}} 2NH_3 + H_2CO_3 \quad (1)$$

In 1995, Atwater et al. immobilized urease in diatomaceous earth, while urea was continuously fed into the bioreactor and the byproducts were discarded.[9] This electrochemical cell will be able to oxidize the ammonia molecules in solution to extract up to six electrons for every two ammonia molecules (eq 2) and producing molecular nitrogen and water.

$$2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^- \quad (2)$$

Ammonia has been considered suitable to be used as an alternative fuel due to its high energy density (12.6 MJ L^{-1}) and ease of storage and transportation in comparison to hydrogen.[10] For this reason, recent work with electrolyzers[11,12] and microreactors[13] has focused on the development of a catalyst[13−16] to produce fuel by converting ammonia to hydrogen or by using a direct ammonia fuel cell device.[17] Hence, the results of this research have broad applicability to wastewater treatment and alternative energy generation applications.

EXPERIMENTAL SECTION

Materials and Equipment. A total organic carbon (TOC) analyzer from Shimadzu Co. model 5000 A was used to determine the amount of organic carbon in the liquid samples. Coconut shell GAC used in this experiment was purchased from Calgon Carbon Corporation. Urea (ACS reagent, 99–100.5%), urease (E.C.3.5.1.5, from *Canavalia ensiformis* (Jack bean) Type VII; initial activity of 400,000–800,000 units/g solid), potassium phosphate monobasic (KH_2PO_4), potassium phosphate dibasic (K_2HPO_4), sulfuric acid (H_2SO_4, TraceSELECT Ultra, ≥95% (T)), nitric acid (HNO_3), hydrochloric acid (HCl), potassium chloride (KCl), potassium hydroxide (KOH), potassium ferricyanide ($K_3Fe(CN)_6$), potassium ferrocyanide ($K_4Fe(CN)_6$), ammonium sulfate ($(NH_4)_2SO_4$), phenol-nitroprusside, alkaline hypochlorite, and potassium hexachloroplatinate IV (K_2PtCl_6, 99.99+ % trace metals basis) were all purchased from Sigma Aldrich (U.S.A.) and used without further purification. An SP-50 potentiostat/galvanostat from BioLogic U.S.A., along with a common glass three-electrode cell system was used for all the electrochemical procedures. The boron-doped diamond (BDD) substrate (Element 6, 0.038–0.105 Ω, [B]: 10^{20} cm^{-3}) was used as the working electrode, Ag/AgCl (0.197 vs NHE) as the reference electrode, and a platinum wire as the counter electrode with constant N_2 purging. An UV–vis spectrophotometer was also used along with a 1 cm path length quartz cuvette.

Immobilization of Urease on Granulated Activated Carbon. First, the GAC material was washed thoroughly with ultra pure water (Barnstead 18.5 MΩ), followed by overnight drying at 100 °C in a conventional oven. Thereafter, a urease stock solution was prepared, and different quantities were used in concentrations ranging from 0.1 to 2.0 mg/mL and transferred to 2 mL eppendorf vials containing 25 mg of the GAC samples while maintaining the volume constant by completing with sodium phosphate buffer solution (PBS). Then, the samples were allowed to equilibrate in a shaker table at 150 rpm for 2 h. Afterward, the unadsorbed protein was subtracted to determine the urease concentration. The BCA colorimetric assay kit from Pierce Biotechnology was used to determine the amount of unadsorbed protein in the supernatant and, thus by difference, the amount adsorbed. A total of three washes were made with PBS to account for any loosely adsorbed protein in the material.

Urease Enzymatic Activity. The activity of the urease in solution was determined following the protocols reported by Weatherburn[18] and Ghasemi et al.[19] with minor modifications. All reactions were carried out in 100 mM potassium phosphate buffer at ambient temperature at the indicated pH and 333 mM of urea solution (i.e., 13,000 ppm urea, 8,000 ppm NaCl, and 1700 ppm KCl). The urea solution was prepared with specific quantities to mimic human urine concentrations.[20] The reaction was initiated by the addition of 100 μL of enzyme to 900 μL of urea solution. The final enzyme concentration was 0.05 mg/mL (0.1 μM). To quantify the amount of produced ammonia, 50 μL aliquots of the above reaction were taken at different time points. This aliquot was added to 500 μL of phenol-nitroprusside and 500 μL of alkaline hypochlorite and vortexed. The mixture was incubated at 37 °C for 15 min. Then, the absorbance was measured at 630 nm, and the amount of ammonia was determined by the use of a standards calibration curve. This assay was conducted at a urea solution pH of 7.4.

After the determination of the initial activity in solution, the residual enzymatic activity of the GAC–urease composite was determined for samples containing 25 mg of GAC and 2.0 mg/mL of urease immobilized, as described previously. The GAC–urease composite was dissolved in 100 μL of PBS and 900 μL of urea solution to initiate the reaction. Then, 50 μL aliquots of the above reaction were taken at different time points. This aliquot was added to 500 μL of phenol-nitroprusside and 500 μL of alkaline hypochlorite and vortexed. The mixture was incubated at 37 °C for 15 min. Then, the absorbance was measured at 630 nm, and the residual activity was calculated as a percentage.

Electrochemical Cell. In order to be able to oxidize the ammonia molecules present in solution, platinized boron-doped diamond electrodes were fabricated following published procedures.[21] After the electrodes were prepared, urea, ammonia, and buffer electrochemical profiles were recorded in order to be able to identify the characteristic signals under the conditions of the bioreactor. Namely, a solution of 0.1 M ammonia, 0.1 M urea, and 100 mM phosphate buffer at a pH of 8.3 was prepared, and cyclic voltammetry was recorded. Solutions were poured into the electrochemical cell. The potential was scanned from −0.6 to 1.0 V vs Ag/AgCl at a scan rate of 25 mVs^{-1}, and the generated current density was measured.

Initial Wastewater Feed and Osmotic Agent Samples. For the bioreactor experiments, two different types of samples were used: the wastewater feed and the osmotic agent (OA).[8] The wastewater feed consisted of urine and hygiene wastewater with humidity condensate simulant. Actual urine was collected from male volunteers at NASA Ames Research Center (NASA ARC) and stored at 4 °C until use. Humidity condensate was prepared according to the Ersatz formulation.[22,23] Hygiene water was collected from shower water of both male and female volunteers using No-Rinse Body Wash. The wastewater feed solution was processed through a FO/RO system from NASA ARC.[24−25] The OA samples were obtained from the Osmotic Agent tank of the FO/RO system. The OA samples contain approximately 10−30g/L of NaCl. Both the feed and the OA solutions were allowed to react for 4 h with the bioreactor. The supernatants were then extracted for use in the electrochemical cell.

Urea Bioreactor/Electrochemical Cell (UBE) Experiments. For the bioreactor experiments, 10.0 g of GAC was placed in a 250 mL glass bottle containing 150 mL of 2 mg/mL of urease solution at pH 7.4 and allowed to equilibrate for 2 h in a shaker table. Thereafter, the adsorbed protein was determined as previously described. and the GAC−urease composite was washed three times with PBS buffer. Then, 50 mL of urea solution was poured in the GAC−urease bioreactor to initiate the enzymatic reaction. Subsequently, 10 mL aliquots were withdrawn at 1, 4, and 72 h of reaction. The same procedure was applied for both the wastewater feed and OA samples. All these samples were tested on the electrochemical cell to electrooxidize the dissolved ammonia in the solution. The ammonia content on each sample was measured as previously described, while the urea concentration, before and after the treatment, was quantified by the use of the QuantiChrom Urea Assay Kit (DIUR-500) from BioAssay Systems. A TOC analyzer was used as a water quality parameter. TOC was recorded before and after the bioreactor reaction.

RESULTS AND DISCUSSION

Assessment and optimization of UBE system. First, the enzyme urease was immobilized onto GAC at a pH of both 7.4 and 8.3 in a phosphate buffer solution to test possible pH dependency. The immobilization process was carried out at room temperature for 2 h and the results are presented in Figure 2. This figure shows that only slight differences are observed in the immobilization of urease into GAC at both pH values. Therefore, pH 7.4 was selected for any further immobilization to the protein's optimum pH. In this way, the possible residual activity of the enzyme is maximized.

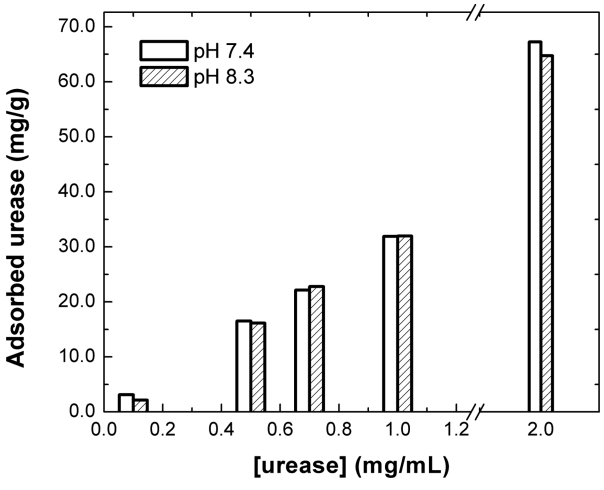


Figure 2. Urease immobilization into GAC at pH 7.4 (white) and pH 8.3 (dashed) after 2 h at room temperature. Adsorbed urease (mg/g) as a function of urease initial concentration ranging from 0.1 to 2.0 mg/mL.

Once the urease−GAC composite was constructed at pH 7.4, the immobilized enzyme activity was measured. For instance, 36% of residual activity was obtained in comparison to the enzyme free in phosphate buffer solution. This decrease in enzyme activity is possibly due to protein denaturation when in contact with the GAC hydrophobic core. However, when the residual activity of the immobilized enzyme is measured after two weeks, 97% of the urease−GAC initial activity is retained. These findings indicate that the GAC structure is suitable for the immobilization of the protein urease and that long-term activity can be achieved. Previous investigations with urease in petroleum-based spherical activated charcoal found that about 20% of the carbon pores are enzyme occupied and high residual activities are obtained. The reason for high residual activities is ascribed to the similarities between the structure provided by the carbon material, and the membrane-based pockets that hold proteins in their natural state.[26]

Once the initial conditions for the GAC−urease composite were investigated, the GAC−urease system (i.e., urea bioreactor) was scaled-up for the actual urea bioreactor experiments. For the initial urea bioreactor experiments, a urea solution (containing analytical quantities of 13,400 mg/L urea, 8001 mg/L of sodium chloride, and 1641 mg/L of potassium chloride) was used to perform a contact time experiment. These components were selected to mimic the main chemicals and quantities found in humane urine.[20] Therefore, two urea bioreactors (and two blanks) were set. After 1 and 4 h of enzymatic reaction with the urea solution, the supernatants were withdrawn, and the amount of ammonia produced was measured. The results revealed that after 4 h, 379 mg/mL of ammonia was produced (pH 9.3), resulting in 40% higher ammonia concentration than the 1 h reaction (pH 8.9). Moreover, a 72 h experiment was also performed, and the ammonia concentration resulted in 231 mg/mL, suggesting that after certain period of time the ammonia molecules are readsorbed from the bulk solution by the granulated activated carbon. These supernatants were also used to test the electrochemical cell system behavior after the bioreactor step.

Before evaluating the ammonia-containing samples from the bioreactor, a series of standards for urea, ammonia, and buffer were submitted to the electrochemical cell system. Cyclic voltammograms presenting the current density (i.e., mA/cm^2) as a function of voltage (i.e., V vs Ag/AgCl) for a 0.1 M urea solution, 0.1 M ammonium sulfate solution, and 0.1 M phosphate buffer solution all at pH 8.3 were performed (Figure 3). Such pH was selected as an intermediate value between the enzyme optimum pH and the final pH values observed in the bioreactors. From this figure, a peak signal appearing at about 0.10−0.20 V vs Ag/AgCl for the ammonium sulfate solution (Figure 3a) is ascribed to the ammonia electro-oxidation. The refereed peak was not observed for the buffer solution (Figure 3b) nor the urea solution (Figure 3c), which further confirms the previous results.

The cyclic voltammogram for the bioreactor samples (i.e. bioreactor product) after 1 and 4 h of contact with the urea solution (i.e., containing analytical quantities of 13,400 mg/L urea, 8001 mg/Lsodium chloride, and 1641 mg/L potassium chloride) were performed and are shown in Figure 4.

It is observed from this figure that the appearance of an electrochemical signal at about 0.1 V vs Ag/AgCl is ascribed to the electrooxidation of ammonia. It is clear that a 4 h (Figure

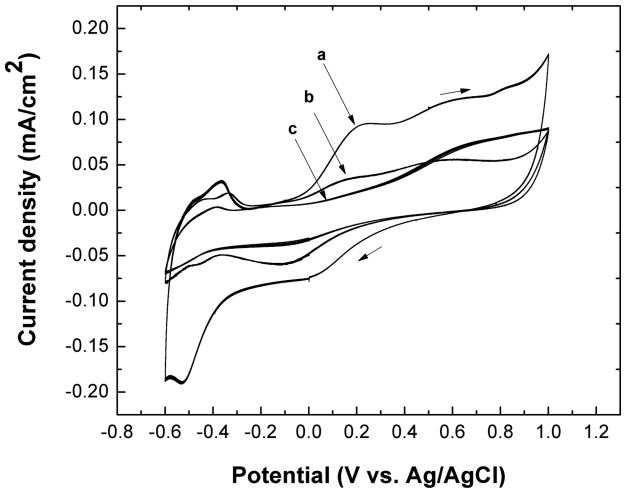


Figure 3. Cyclic voltammogram of (a) 0.1 M ammonium sulfate, (b) 0.1 M urea solution, and (c) phosphate buffer solutions at pH 8.3 over Pt-BDD electrodes at 25 mV/s vs Ag/AgCl.

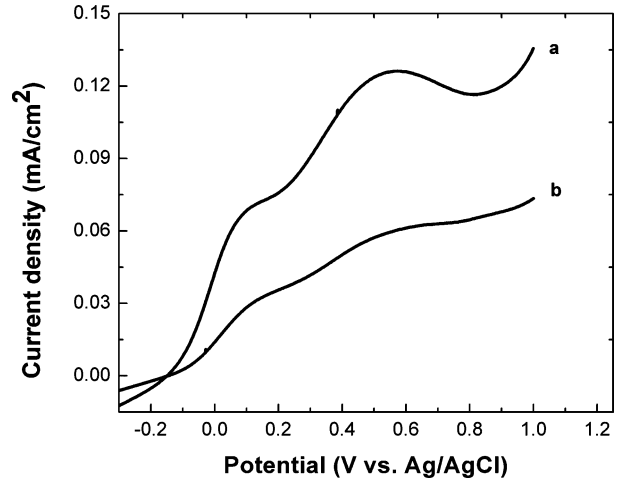


Figure 4. Linear polarization for the bioreactor product at 4 (a) and 1 h (b). Bioreaction was carried out in a solution of 13,400 mg/L urea, 8001 mg/L sodium chloride, and 1641 mg/L potassium chloride at pH 7.4 in Pt-BDD electrode at 25 mV/s. pH after bioreaction is 8.9 and 9.3 for 1 (oxidation charge = 0.040 mC) and 4 h (oxidation charge = 0.14 mC), respectively.

4a) period of contact time promotes the formation of ammonia molecules, which results in higher current densities. The 3 h difference represents a 40% increment in the ammonia electrooxidation current. This is consistent with the difference in concentration of aqueous ammonia measured previously at 1 and 4 hours of reaction. Therefore, a 4 h reaction time of the urea containing solution with the bioreactor is selected for further experiments.

3.2. Bioreactor Effectiveness. Table 1 lists the analytical quantities of urea, ammonia, and TOC for each sample before and after treatment in the bioreactor. From this table, it is noticeable that 22% and 57% of urea removal was achieved for the feed and OA solutions, respectively, after the bioreaction. These results suggest that the 22% urea removal in the feed samples represents the contribution of adsorbed urea into the empty spaces of the GAC and the enzymatic hydrolysis of urea. However, it can also be noted that ammonia production (i.e., urea recovery) was not achieved. This may be the consequence

Table 1. Summarized Results for UBE System[a]

component		bioreactor feed (mg/L)	bioreactor effluent (mg/L)	% urea and TOC removal or NH_3 produced
wastewater feed	urea	15,946	12,434	22
	ammonia	10,541	10,416	1
	TOC	4769	912	81
osmotic agent	urea	204.6	87.9	57
	ammonia	87.6	145.8	34
	TOC	2491	464.6	81

[a]Urea concentration (mg/L), ammonia concentration (mg/L), and total organic carbon (mg/L) in the bioreactor feed and bioreactor effluent for both the wastewater feed and OA solutions.

of an extreme enzyme degradation or inactivation due competitive inhibition with other chemicals present in the feed solution. Conversely, for the OA samples, the urea removal was 57%, accompanied by an ammonia production of 34%. For instance, the difference between the initial ammonia concentration from the OA solution and after the bioreactor is 58.2 mg/mL, which is ascribed to come from the bioreactor process (i.e., urea degradation to ammonia). Hence, if the urea removed (116.7 mg/L) from the OA solution is assumed to be all converted to ammonia in the bioreactor, then 66.0 mg/L NH_3 must be present after the bioreactor process (i.e., taking the molar masses and stoichiometey between both compounds), which provides the bioreactor an efficiency of 88% for the degradation of urea to ammonia when employing the OA solution.

Figure 5 shows the results for the electrochemical cell. Figure 5a represents the electrochemical oxidation of the OA solution,

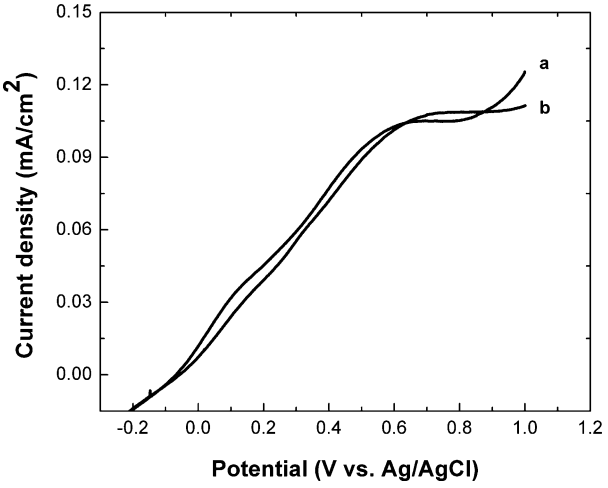


Figure 5. Linear polarization for the bioreactor product after forward osmosis for the osmotic agent solution (oxidation charge = 10.3 μC) sample (a) and bioreactor feed (oxidation charge = 1.1 × 10^{-3} μC) solution (b) after 4 h of bioreaction in Pt-BDD electrode at 25 mV/s.

where an oxidation signal can be observed at about 0.1 V vs Ag/AgCl, which corresponds to the ammonia electrooxidation. The experimental charge transferred during this electrochemical oxidation process is 10.29 μC/cm^2. In contrast, the feed cyclic voltammogram (Figure 5b) shows nearly no current generation, even when the analytical amount of ammonia in this sample is 10,416.5 mg/L, which clearly suggest a fouling process occurring in the catalysts. These results suggest that the feed solution contains components that make this step

dx.doi.org/10.1021/sc400342x | ACS Sustainable Chem. Eng. 2014, 2, 749−754

unsuitable for the UBE system. However, the UBE system would be ideal for the OA solution to achieve higher efficiency.

Finally, the TOC before and after the bioreactor process was determined for the feed and OA solutions (Table 1). As observed, after the bioreactor process, TOC concentration is reduced to about 10% in the OA solution. The results show that the ideal place to the biofuel cell reactor is at the OA tank where optimum urea removal is obtained.

CONCLUSIONS

This work presented the proof-of-concept for a Urea Bioreactor Electrochemical (UBE) system to achieve resource recovery from water recycling systems. A GAC−urease bioreactor was used to recover urea from the wastewater stream and convert it to ammonia. Then, the ammonia produced was used to feed an electrochemical cell to generate electrical energy. The results of this work showed the feasibility of using the UBE system in combination with a forward osmosis subsystem for water reclamation. The UBE system in combination with the FO system presented an overall efficiency higher than 80% for the removal of organic carbons. The urea recovery with the GAC−urease system was shown to be 86%. This system provides a method of targeting urea and removing it as N_2 while generating electrical current. The samples used for the bioreactor were obtained from a membrane-based FO/RO system. However, the results showed that the UBE system could be used in any wastewater treatment systems containing urea and/or ammonia. Since this work, a scale-up UBE system has been designed and tested for use with the Forward Osmotic Secondary Treatment at NASA ARC.[24]

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported in part by the NASA Center for Advanced Nanoscale Materials under Grant NNX08BA48A, NNX13AD20A, and the NASA Graduate Student Researchers Program under Grant NNX08AV42H. The authors are also grateful to David Beeler for comments and editing and Kevin Howard.

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