

Recovering Nitrogen as a Solid without Chemical Dosing: Bio-Electroconcentration for Recovery of Nutrients from Urine

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Supporting Information

ABSTRACT: This letter presents the proof of concept of a novel bio-electroconcentration system (BEC), a hybrid microbial electrolysis/electrodialysis cell specifically designed to recover nitrogen (as ammonia NH₄-N), phosphorus (as phosphate PO₄-P), and potassium (as K⁺) from urine. Using a synthetic urine medium, the BECs could reach high current densities of up to 37.6 A m⁻² at E_{we} values of 0.0 versus the standard hydrogen electrode (SHE) and 50 A m⁻² at 0.2 V versus SHE, which in turn drove the removal and recovery of N, P, and K at rates of 7.18 kg of NH₄-N m⁻³ day⁻¹, 0.52 kg of PO₄-P m⁻³ day⁻¹, and 1.62 kg of K⁺ m⁻³ day⁻¹ into a concentrate stream (containing 1.87 M NH₄-N, 0.29 M PO₄-P, and 0.18 M K⁺). Finally, this communication



demonstrates the recovery of a nitrogen-rich solid from the synthetic urine (in the form of pure NH_4HCO_3 crystals with 17% N content) without any chemical additions via the flash-cooling of the produced nutrient-rich concentrate to 4 °C. These two new products may help facilitate the reuse of urine nutrients in the fertilizer or protein production industries of the future.

INTRODUCTION

The removal and recovery of nutrients from waste streams are considered paramount in helping to meet the emerging environmental health and food needs of a booming global urban population.^{1,2} Currently, the main nutrient components in fertilizers, nitrogen (N), phosphorus (P), and potassium (K), are sourced in an unsustainable manner through fossil energyintensive or mining processes from limited ore supplies, compromising their future availability.^{3,4} However, these nutrients are abundant in waste streams and particularly in human urine, which contributes 79% of the N, 47% of the P, and 71% of the K in domestic wastewater, making it an ideal macronutrient source.^{5,6} Nevertheless, urine accounts for only \sim 1% of the total volume in domestic wastewater, therefore necessitating source-separation technologies and adequate processes that can recover these nutrients in a sustainable manner.^{2,7}

Recently, pioneering works by Kuntke et al.^{8,9} and Tice and Kim¹⁰ have demonstrated that microbial electrochemical technologies (METs) can be technically and economically feasible for nitrogen removal and recovery ($N_{R\&R}$) from source-separated urine. This is due in part to the ideal properties of urine for MET applications (high COD, electric conductivity (EC), and buffering capacity),⁶ which has allowed for the production of current densities of up to 23.1 A m^{-28,11} and a maximal $N_{R\&R}$ rate of 0.52 kg of N m⁻³ day⁻¹ (as ammonia).¹²

This communication presents the proof of concept of a novel MET that aims to contribute to the chemical-free and self-sustaining recovery of N, P, and K from source-separated urine

by demonstrating the possibility of producing a concentrated liquid ($\geq 2.6\%$ N, $\geq 0.9\%$ P, and $\geq 0.7\%$ K) and a solid product (17% N) from synthetic urine.

MATERIALS AND METHODS

Reactor Design. The experiments were conducted in triplicate electrochemical reactors over approximately 2 years of laboratory work. Each flat plate-type reactor consisted of three 200 cm³ [10 cm (width) \times 10 cm (height) \times 2 cm (depth)] chambers (hereafter described as anodic, concentrate, and cathodic compartments) separated by a 100 cm² cationexchange membrane (CEM, CMI-7000) and an anionexchange membrane (AEM) with the same dimensions (AMI-7001, Membranes International) in a manner analogous to that of electrodialysis,¹³ as shown in Figure 1A. Each anodic electrode consisted of 165 g of plain graphite granules (EC-100, Graphite Sales) with two 14 cm long plain graphite rods embedded as current collectors (Ø5 mm, Element14). The cathodes were made of the same amount of granules but with an 81 cm² titanium mesh (Advent research materials) as a current collector.

BEC Principles of Operation. BEC reactors concentrate nutrients from urine by using an electric field that drives charged species across ion-selective membranes, as in electro-

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Figure 1. BEC configuration. (A) Schematic diagram of the experimental setup, with flows of electrolyte, gas, current, and ionic species across cationand anion-exchange membranes (CEM and AEM, respectively). (B) Photograph of the experimental setup with triplicate BEC bioreactors.

dialysis (see the configuration in Figure 1A). In BECs, this field is generated primarily by electroactive bacteria (EAB) catalyzing the anaerobic oxidation of urine organics (e.g., acetate in eq 1), with the electric circuit closed at the cathodic electrode by applying a small amount of energy to drive hydrogen evolution (eq 2) as in microbial electrolysis cells (MECs).¹⁴ At steady state, BEC reactors exhibited working pH values of 6.8 \pm 0.4, 7.8 \pm 0.4, and 8.4 \pm 0.4 for the anodic, concentrate, and cathodic compartments, respectively, which allows for the exploitation of the acid/base NH_4^+/NH_3 (eq 3) and $CO_2/HCO_3^{-}/CO_3^{2-}$ (eq 4) equilibria (i) to drive the protonation of free ammonia NH₃ (FA; present in hydrolyzed urine because of urea breakdown), resulting in the formation of NH_4^+ (eq 3), which is subsequently utilized as the main proton shuttle leading to its removal and recovery,^{9,15} and (ii) to produce bicarbonate (HCO_3^{-}) from CO_2 at the cathode (given the CO_2 equilibrium in eq 4¹⁶), which, besides buffering the cathode compartment, acts as the main counterion to preserve electroneutrality, thereby also accumulating in the midcompartment as the principal anion. Recent investigations have shown that VFAs (e.g., acetate) can compete with HCO₃⁻ for migration,¹⁷ which in the case of the BEC could lead to undesired contamination of the concentrate. Accordingly, an aerated 200 cm³ column filled with biofilm carriers (Anox-Kaldnes K1) was strategically placed after the anodic compartment, increasing the total working reactor volume to 600 cm³, to degrade the organic acids and prevent their accumulation.

$$CH_3COO^- + 2H_2O \rightarrow 2CO_2(aq) + 7H^+ + 8e^-$$
 (1)

$$8e^- + 8H^+ \to 4H_2 \tag{2}$$

$$H^{+} + NH_{3}(aq) \rightleftharpoons NH_{4}^{+} \quad pK_{a} = 9.25$$
(3)

$$2CO_{2}(aq) + 2H_{2}O \rightleftharpoons 2HCO_{3}^{-} + 2H^{+} \rightleftharpoons 2CO_{3}^{2-} + 4H^{+}$$
$$pk_{1} = 5.84; pk_{2} = 8.96$$
(4)

A final operational consideration is that the ionic migration across the CEM and AEMs resulted in a concomitant osmotic/ electroosmotic flow,^{13,18} which led to the continuous production of new concentrate that was recovered as an overflow, without the need for pumping (see Figure 1A).

Experimental Operation. The synthetic urine medium utilized [aiming to replicate source-separated and hydrolyzed human urine (see the full composition in the Supporting Information)],^{19–21} with a pH of 9.2 ± 0.2 and an EC of 19.5 ± 0.5 mS cm⁻¹, was supplied at a rate of 1.48 L day⁻¹ after natural settling of precipitates in the feed tank. To achieve good mixing, recirculation was performed at a rate of 20 mL min⁻¹ for each compartment, thus avoiding pressure inequalities between them. Finally, the reactors were also equipped with a secondary recirculation pump, activated by a pH-relay controller programmed to maintain the anode effluent pH between 7.10 and 7.25 (R1 mode) and between 7.20 and 7.35 (R2 mode), by recirculating the catholyte at a rate of 10 mL min⁻¹ back into the anodic compartment (see Figure 1A).

Each reactor was operated in chronoamperometric (CA) mode as a microbial electrolysis cell (MEC) using a potentiostat (Bio-Logic VMP-3), with the anode as the working electrode (WE) at a potential E_{WE} of 0.0 V versus the standard hydrogen electrode (SHE), the cathode as the counter electrode (CE), and a 3.5 M Ag/AgCl electrode (BASi, USA) as a reference.¹ To further characterize the EAB activity, cyclic voltammetry (CV) was performed using a VersaSTAT 3 potentiostat (Princeton Applied Research) to scan E_{WE} potentials from -0.4 to 0.4 V versus the SHE at 1 mV s prior to inoculation (blank) and after reaching peak performance. For all CA/CV tests, the electrical output (in milliamperes) was normalized to the CEM/AEM surface area (100 cm^2) , rather than a specific electrode surface, to provide a better reference toward upscaling, irrespective of specific electrode materials.

Moreover, a data acquisition/control module (Agilent 34972A-LXI; Element14) was utilized to monitor the reactor's total cell voltage and the pH of the electrolyte at the outlet of the anodic chamber (see Figure 1A) and to furthermore act as a



Figure 2. BEC performance. (A) BEC chronoamperometric operation at 0.0 vs the SHE in various cathode-to-anode recirculation modes: RO, no pH-relay recirculation; R1, pH-relay recirculation within the pH range of 7.10–7.25; R2, recirculation between pH 7.30 and 7.45. (B) Cyclic voltammograms for a blank (graphite granules prior to inoculation, red) and the enriched consortium (green). (C) Midcompartment up-concentration of key species NH_4 -N, Na^+ , K^+ , PO_4 -P, and total inorganic carbon (TIC) and electric conductivity (EC) vs time at an average current density of 29.3 A m⁻² with R2 recirculation settings.

pH relay, controlling the actuations of the secondary recirculation pump within the aforementioned pH intervals.

All experiments were conducted at room temperature (22.0 \pm 2.5 °C).

Inoculation, Enrichment, and Community Analyses. Each reactor was seeded with a concentrated mixed inoculum derived from three sources: an acetate-fed bioanode, a urinal, and anaerobic digester sludge. Each of the tree sources was sampled for 200 mL, pelleted at 4000 rpm for 1 h, and then resuspended to 1 mL in phosphate-buffered saline (pH 7.2). The three resuspended concentrates were subsequently homogenized into 3 mL using a vortex, and each reactor received 1 mL of this complex mixture as an inoculum. The biomass was progressively adapted to increasing ammonia concentrations for 16 weeks. Once successfully enriched, biofilms were extracted from the graphite granules and their 16S-rRNA was amplified, sequenced, and processed as previously described.^{22,23}

Chemical Analyses. As shown in Figure 1B, each reactor setup had 13 sampling ports to allow for constant monitoring at all compartment inlets and outlets. Samples (100 μ L) were regularly taken to monitor pH and conductivity (EC) throughout the entire process using specialized microprobes (LAQUAtwin, Horiba) that were calibrated prior to each measurement. Moreover, 0.22 μ m-filtered samples were analyzed in triplicate with standard potassium dichromate kits for COD (Merck-Millipore) and via inductively coupled plasma optical emission spectrophotometry (ICP-OES), flow-injection analysis (FIA), and near-infrared detection (NIRD) to determine the concentrations of NH₄-N, Na⁺, K⁺, PO₄-P, and total inorganic carbon (TIC) across the system (see methods details in refs 22 and 24). Furthermore, during nutrient accumulation, concentrate samples were taken every 12 h and analyzed in triplicate by ICP, FIA, and NIRD.

Nutrient Removal and Recovery Estimations. Once the maximal up-concentration levels had been attained, the reactors were operated at the same feed rates and R2 mode. COD removal and the nutrient removal and recovery rates for NH_4 -N, PO_4 -P, K^+ , and Na^+ were averaged over four replicate runs of 72 h per reactor and subsequently normalized with regard to their loading rates and total reactor volume (600 cm³). The removal and/or recovery efficiencies (in percent) were calculated by comparing total influent and effluent concentrations for each target nutrient, while the BEC's Coulombic

efficiency (CE) was calculated following the method of Logan et al.²⁵ To determine the fraction of NH₄-N that could be recovered as a solid, the concentrate recovered in the external collection bottle (see Figure 1A) from the same four independent 72 h accumulation runs mentioned above was flash-cooled to 4 °C for 20 min by using a refrigeration coil (RC1, Ratek) to lower the supersaturation boundary of NH₄HCO₃, resulting in the formation of crystals. To verify their composition and recovery fraction contribution, these crystals were dissolved with 5 M HCl and analyzed via FIA, ICP, and NIRD. Finally, they were also analyzed by XRD and Raman spectroscopy, using established methods previously described,^{26,27} to confirm their structure.

Letter

RESULTS AND DISCUSSION

After successful enrichment of an electroactive community on the synthetic urine medium, the reactors were operated with a continuous supply rate of 1.48 L day⁻¹. At this rate, the BEC output averaged 26.6 \pm 0.5 A m⁻² at a cell voltage of 1.40 V without cathode-to-anode recirculation (see R0 in Figure 2A). When the R1 mode was utilized [anodic effluent at pH 7.10– 7.25 (see R1 in Figure 2A)], the output increased to 27.3 \pm 1.3 A m⁻². Finally, when the recirculation was set to R2 mode [pH 7.30–7.45 (see R2 in Figure 2A)], the output was further enhanced to a maximum of 37.6 A m⁻² and an average of 29.3 \pm 2.3 A m⁻² (at 1.46 V), which are the highest current densities reported to date for an ammonia removal and recovery system of the MFC/MEC type, irrespective of materials or configuration (see a comprehensive comparison in ref 11).

The ability to reach even higher output levels was confirmed by leaving the recirculation pump on and performing CV, with currents of up to 45.2 A m⁻² attained at an E_{WE} of 0.0 V versus the SHE and a peak of 50.6 A m⁻² at 0.2 V versus the SHE, while the abiotic control exhibited <0.5 A m⁻² at the same potential (see Figure 2B). Unfortunately, such high currents exceed the limits of the BioLogic galvanostat mode (maximal continuous current of 400 mA, i.e., 40 A m⁻²), so the reactors have not been operated under such high-current conditions for this very first examination of the BEC concept.

While the system was operated at the same supply rate of $1.48 \text{ L} \text{ day}^{-1}$ in R2 recirculation mode, the COD removal rate, Coulombic efficiency, and up-concentration profiles of key nutrients in the concentrate compartment were calculated. Given that the synthetic urine medium utilized was not



Figure 3. Nutrient removal and recovery balances and characteristics. (A) Elemental balances for N, P, K, and Na recovered and/or unrecovered by the BEC reactors at an average of 29.3 A m⁻² and 1.48 L of urine day⁻¹. Error bars show the standard deviation. (B) Stereoscopic micrograph of the produced crystals. (C) XRD spectrum of the produced crystals, with known peaks for NH₄HCO₃ marked in blue. (D) Raman profiles for the crystals obtained by the BEC process (red) vs high-purity NH₄HCO₃ crystals from a commercial supplier (blue).

sterilized (see the Supporting Information), the average influent COD concentration was 7.36 ± 0.17 g of COD L⁻¹, lower than the theoretical COD of the 140 mM acetate utilized in the formulation, which corresponds to a loading rate of 18.06 ± 0.41 kg of COD m⁻³ day⁻¹. Of this, only an average of $17.02 \pm 2.99\%$ was found to be removed by the anodic process, resulting in a relatively low COD removal rate of 3.07 ± 0.54 kg of COD m⁻³ day⁻¹, indicating that the BECs were limited by buffering capacity and not by COD.⁶ Nevertheless, the Coulombic efficiency was found to be 94.43 \pm 16.63%, meaning that the BECs did transduce the vast majority of the chemical energy of the COD processed as electric charge transfer.

With regard to nutrient recovery, Figure 2C demonstrates that it is possible to up-concentrate key nutrients "from scratch" in this compartment using the BECs' electric field as a driving force, with maximal up-concentration levels reached after approximately 5.5 days in line with the measurable changes in EC, which peaked at $114.2 \pm 1.6 \text{ mS cm}^{-1}$. Of primary interest, the NH₄-N was successfully up-concentrated to reach 1.87 \pm 0.02 M or 26.2 g of NH₄-N L^{-1} (×4.45 ± 0.04 times vs feed concentration). The second most abundant species recovered was TIC, predominantly in the HCO_3^- form (based on eq 4) and the working pH of 7.8 \pm 0.4 in the midcompartment), reaching 1.85 ± 0.01 M after 5.5 days. Simultaneously, the other key ionic species were also recovered in the concentrate but at notably inferior concentrations, because of their lower concentrations in the feed and the differential fluxes for ionic species across CEMs and AEM, $s^{13,28}$ reaching 0.29 \pm 0.01 M (×12.22 \pm 0.25 times up-concentration) for PO₄-P, 0.18 \pm 0.01 M ($\times 3.77 \pm 0.08$) for K⁺, and a much lower value of 0.17 \pm 0.01 M (× 1.83 \pm 0.03 times up-concentration) for Na⁺.

Once the BEC concentrate reached the peak values mentioned above, the reactors were operated at the same supply/recirculation rates to establish the N, P, K, and Na balances and recovery rates at steady state. Figure 3A shows that under steady-state conditions, 59.7 \pm 2.47% of the nitrogen (as NH₄-N) was removed from the anodic compartment, resulting in a prospective $N_{R\&R}$ of 8.67 kg of NH₄-N m⁻³

day⁻¹; however, the level of NH₄-N measured in the cathode chamber was always higher than the values observed in the anode effluent, indicating that the AEM allowed the permeation of approximately $10.2 \pm 0.7\%$ of all the nitrogen recovered, probably because of insufficient perm-selectivity (90% according to the manufacturer), the very high concentration gradients between the concentrate and feed, and the migration of paired and/or uncharged N species such as NH₃. Accordingly, the effective N recovery efficiency was 49.5 \pm 1.8%, corresponding to an $N_{R\&R}$ of 7.18 kg of NH₄-N m⁻³ day⁻¹, which is nevertheless the highest reported value for nitrogen removal and recovery for METs to date (see a review by Kelly and He²⁹). On the basis of this effective $N_{R\&R}$, the BEC working voltage (average of 1.46 V) and current density (average of 29.3 A m⁻²), the specific energy required for $N_{R\&R}$ was estimated to be 8.58 MJ (kg of NH_4-N)⁻¹ [2.38 kWh (kg of NH_4-N)⁻¹], albeit recovered as a liquid product with only 2.62% (w/w) nitrogen.

Each BEC reactor additionally recovered an average of. 42.8 \pm 1.0% of the phosphorus ($P_{\rm R\&R}$ of 0.52 kg of PO₄-P m⁻³ day⁻¹), 54.7 \pm 1.3% of the potassium ($K_{\rm R\&R}$ of 1.62 kg of K⁺ m⁻³ day⁻¹), and 51.9 \pm 1.2% of the sodium (Na_{R&R} of 2.20 kg of Na⁺ m⁻³ day⁻¹) supplied. For these ions, there was no measurable AEM leakage, possibly because of their lower concentrations.

Finally, flash-cooling the concentrate resulted in the formation of the relatively large (\geq 500 μ m) crystals pictured in Figure 3B. XRD analysis of these (Figure 3C) returned characteristic peaks for NH₄HCO₃, indicating the presence of the target product, as further confirmed by the Raman spectra (contrasted against a known spectrum³⁰ and by analyzing pure NH₄HCO₃ crystals) shown in Figure 3D. The formation of these NH₄HCO₃ crystals accordingly resulted in an additional solid N_{R&R} fraction, which accounted for approximately one-third of the N recovered (see Figure 3A), meaning that a sizable part of the N recovered remained in solution. Nevertheless, the solid N recovered accounted for a significant N_{R&R} efficiency of 14.30 ± 0.8%, corresponding to 2.07 kg of N m⁻³ day⁻¹ as solid ammonium bicarbonate crystals. To obtain this solid nitrogen, a

preliminary estimation yields a specific energy consumption of 34.23 MJ (kg of NH_4 -N)⁻¹ or 9.51 kWh (kg of NH_4 -N)⁻¹ [based on the electrical and recovery efficiencies mentioned above, a concentrate production rate of 98 mL reactor⁻¹ day⁻¹, a specific heat capacity of 3.9 J K⁻¹ g⁻¹,³¹ a Δ_T of 19 K (room temperature 23 °C, cooling concentrate to 4 °C), and the use of a heat exchanger with a very conservative efficiency of 50%]. If this performance can be successfully up-scaled, BECs could join other more mature technologies for the recovery of nutrients from urine such as nitrification/distillation^{19,32} and struvite precipitation³³⁻³⁷ that are already being piloted outside of the laboratory.

The results for synthetic urine presented here, including the highest current densities and nutrient recovery rates reported to date for urine-fed METs, demonstrate that the novel BEC concept could be a promising technology for recovering and reusing urine nutrients. Nevertheless, significant work is still needed to increase recovery efficiencies (currently $\leq 60\%$), enhance the nutrient titers in the concentrate, and reduce the total level of energy consumption of the process, so that the technology can become economically viable in the near future. To meet these objectives under real-world conditions, an upscaled BEC reactor (50 person equivalent) will be piloted from early 2017 at the Innovation Centre of Queensland Urban Utilities in Brisbane, Australia, using real source-separated urine.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00024.

Synthetic urine medium composition (PDF)

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Notes

The authors declare no competing financial interest.

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