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Effects of operating and design parameters on ion exchange columns for nutrient recovery from urine

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ABSTRACT

Ion exchange is a promising option for recovering nutrients (nitrogen, phosphorus, and potassium) from source-separated urine. We determined that it was feasible to integrate nitrogen and potassium recovery via cation exchange with phosphorus recovery, either via struvite precipitation or anion exchange. Flow rate and intermittent operation did not significantly affect ammonium recovery and adsorption kinetics with Dowex Mac 3, a resin with demonstrated high adsorption density and recovery efficiency. During regeneration, concentration of the sulfuric acid eluent had a more significant effect on performance metrics than did acid flow rate. Nitric acid and hydrochloric acid exhibited similar cation recovery efficiencies as sulfuric acid (>99%); sodium chloride, which has lower costs and environmental impacts associated with its production, exhibited lower recovery efficiencies (77% for ammonium, 88% for potassium). A suite of common pharmaceuticals was used to determine trace organic contaminant fate during adsorption, regeneration, and in the final fertilizer product. Of the ten pharmaceuticals measured, only atenolol and metoprolol were detected in the ammonium sulfate product, both at $<0.1\ \mu g\ L^{-1}$. Ultimately, macronutrients were selectively recovered from urine, which could enable customized fertilizer production.

Water Impact Statement

Ion exchange was used to recover nitrogen, phosphorus, and potassium from urine. This approach aims to remove nutrients at lower cost and energy than treating combined wastewater, while also generating fertilizer. The process was robust over varying flow rates, influent concentrations, and intermittent operation. These promising results provide a basis for evaluating fertilizer production from urine at the pilot scale.

1. INTRODUCTION

Effluent from centralized wastewater treatment plants is a significant source of nutrients, which contribute to the accelerated eutrophication of natural water bodies. Separate collection and treatment of urine at the toilet is a potential alternative to biological nutrient removal at wastewater treatment plants. Nutrients in urine can be removed and recovered to offset energy-intensive synthetic fertilizers.[1] Furthermore, revenue generated from the sale of urine-derived fertilizers could reduce the cost of excreta collection and treatment services. Nutrient recovery from human urine has garnered increasing interest because urine contributes approximately 80% of the nitrogen (N), 50% of the phosphorus (P), and 70% of the potassium (K) load in municipal wastewater streams, but comprises only 1% of the liquid volume.[2]

Several techniques have emerged for recovering either nitrogen, phosphorus or potassium from urine. Phosphorus is often recovered via precipitation of struvite ($MgNH_4PO_4 \cdot 6H_2O$), a slow-release fertilizer.[1,3,4] Anion exchange for phosphorus removal has also been explored.[5] Nitrogen has been recovered from urine using electrochemical separation,[6,7] microbial electrochemical approaches,[8,9] and cation exchange.[10] Thus far, potassium recovery has been preliminarily explored in real urine with limited recovery[12] and in ideal salt solutions with clinoptilolite membranes.[13] These techniques can be combined to recover nitrogen and phosphorus, such as struvite precipitation for phosphorus and cation exchange on zeolite for nitrogen.[11] Combining treatment technologies into a full urine treatment train that recovers nitrogen, phosphorus, and potassium is a logical next step. Ultimately, selective recovery of nitrogen, phosphorus, and potassium could lead to tailored fertilizer production from urine.

Phosphorus recovery by struvite precipitation in urine has been well-characterized in terms of magnesium dosage, mixing, and precipitation mechanisms.[1,14,15] Similarly, equilibrium and kinetic models have been developed for adsorption and regeneration of anion exchange resins.[5,16] In comparison, design and operating parameters have not been optimized for recovering nitrogen from urine via cation exchange, although the approach is a promising option.[10,17,18] In freshly excreted urine, nitrogen is predominately present as urea; during storage, the microbial enzyme urease hydrolyzes urea to ammonium.[19] Cation adsorption can be used to transfer ammonium from urine to adsorbents (e.g., zeolites,[10,20] biochar,[10] loess,[21] ion exchange resins[10]). Once saturated, natural adsorbents can be applied as solid fertilizers; ion exchange resins can be regenerated to produce a concentrated ammonia solution for use as fertilizer or disinfectant.

In a previous study, we compared synthetic and natural adsorbents and demonstrated the recovery of ammonium from urine. The commercial resin Dowex Mac 3 had the highest nitrogen adsorption density (4.23 mmol N g resin^{-1}) and nitrogen recovery efficiency (>99%).[10] While useful for comparing adsorbents and characterizing adsorption isotherms, the batch studies used in the prior study provide limited kinetic information and make it difficult to maintain constant pH,[22] which can impact ammonia speciation and sorption. A more appropriate configuration for implementing ion exchange is a flow-through, fixed-bed reactor. In this study, we used continuous-flow column experiments to investigate the impact of operating conditions (e.g., flow rate, concentration) and other design parameters on adsorption and regeneration of ion exchange resins for all three urine macronutrients (N, P, K).

In addition to nutrients, urine contains trace organic compounds (TrOCs),[23] many of which are contaminants of emerging concern in wastewater treatment because of their deleterious effects on aquatic wildlife[24] and uptake by crops.[25] Several trace organic compounds are present in urine at concentrations 100-10,000 times that of wastewater.[26] While urine separation can effectively reduce input of TrOCs to bulk wastewater, their fate in urine treatment technologies, such as nitrification-distillation,[23] urine storage,[23] electrochemical stripping,[6] and anion exchange,[27] is under investigation. For cation exchange, organic compounds could end up in the urine effluent (which could be discharged to the sewer and go to the wastewater treatment plant), remain in the fertilizer product, or accumulate on the adsorbent. In this study, we investigated the fate of a suite of TrOCs during cation exchange.

During technology development, systems-level analyses can be used to identify knowledge gaps that merit further study at the laboratory scale. In a previous study, we conducted an economic and environmental assessment of household nitrogen recovery using cation exchange, and found that manufacturing of sulfuric acid (used to regenerate the resin) was the major contributor to energy inputs and greenhouse gas emissions.[28] Thus, in the current study we compared alternative regenerants and several metrics of regeneration performance to assess whether these environmental impacts could be reduced.

The overall goal of this investigation was to characterize continuous-flow recovery of macronutrients from urine using ion exchange. While phosphate recovery by anion exchange has been modeled and optimized in batch and continuous regimes,[5,16] nitrogen and potassium recovery from urine via cation exchange have only recently been modeled in batch studies.[21] The

specific objectives of this study were to: (i) demonstrate the feasibility of combined recovery of nitrogen, phosphorus, and potassium, (ii) evaluate the effects of operating conditions (flow rate and concentration) on cation adsorption and regeneration, (iii) compare recovery efficiencies of different regenerants, and (iv) determine the fate of several trace organic compounds during cation exchange. The results are promising and provide a basis for evaluating ion exchange for nutrient recovery at the pilot scale.

2. MATERIALS AND METHODS

2.1 Column setup

Columns were constructed from polyvinyl chloride (PVC) plastic (2.54 cm diameter, 16 cm length unless otherwise noted) and operated in continuous upflow mode for both adsorption (synthetic or real urine influent) and regeneration (H_2SO_4, HCl, HNO_3, or NaCl influent) experiments. For 16-cm length columns, approximate bed volume was 60 mL. The columns were packed with ion exchange adsorbent and coarse sponges at the ends to retain media. Adsorbents were either Dowex Mac 3 (Sigma Aldrich, St. Louis, MO), a macroporous cation exchange resin, or LayneRT (Layne Christensen Co., The Woodlands, TX), an anion exchange resin modified with ferrous oxide nanoparticles (properties in Table S1). For every experiment, column effluent samples were collected regularly (approximately every 20 minutes) and analyzed for inorganic ions (e.g., ammonium, potassium, and phosphate) via ion chromatography, generating breakthrough curves. All experiments were conducted with analytical grade chemicals at room temperature (23 ± 2 °C).

2.2 Combined nutrient recovery

Three treatment trains were compared for combined nutrient recovery: (i) struvite precipitation followed by cation exchange, (ii) anion and cation exchange in series (separate columns), and (iii) simultaneous anion and cation exchange in a mixed-bed column. Ammonium, phosphate, and potassium breakthrough curves were generated for each treatment scheme and compared in terms of bed volumes to 50% breakthrough, slope, and adsorption density. In all setups, real urine was pumped at 4.5 mL min^{-1}. Urine for nutrient recovery was collected from a household urine-diverting toilet in Richmond, California; urine for trace organic analysis was collected from adult volunteers in Berkeley, California. Urine from both sources was stored for several weeks to ensure urea hydrolysis (CPHS protocol 2016-10-9284).

To recover struvite from hydrolyzed urine, $MgCl_2$ was added in a 1.1:1 molar ratio of added magnesium to phosphate in 2 L of urine, based on optimal dosing that has been previously reported.[1] The solution was mixed for 10 minutes and settled for 10 minutes; then the supernatant was pumped into another 2-L bottle, and from there into the cation exchange column. For anion and cation exchange in series, hydrolyzed urine was pumped through first the anion and then the cation exchange column. For both configurations (struvite followed by cation exchange and in-series anion and cation exchange), 1.6 L of urine was pumped at 4.5 mL min^{-1} for 6 hours into each of three replicate columns with no recirculation. For the mixed bed, equal masses of LayneRT and Dowex Mac 3 were mixed dry and added to one 32-cm long column to maintain the same bed volume as all other experiments with 16-cm columns. Due to the longer column for mixed-bed recovery, 3.2 L of urine was pumped for 12 hours at 4.5 mL min^{-1} into each of three replicate columns with no recirculation.

Cation exchange columns with Dowex Mac 3 were pretreated with 10 mL of 1 M borate buffer per gram of resin; LayneRT anion exchange columns were pretreated with 10 mL of pH 12 NaOH per gram of resin. Mixed-bed columns were pretreated with 60 mL of pH 12 NaOH per gram resin to avoid borate sorption to the anion exchange resin. Regeneration solutions were based on previous research, which demonstrated regeneration of Dowex Mac 3 and LayneRT resins with varying volumes of 0.122 M H_2SO_4[10] and 2% NaOH/2% NaCl (0.5 M NaOH/0.342 M NaCl),[22] respectively. Nitrogen and phosphorus recovery efficiencies were compared for these regenerants pumped at 2 mL min^{-1} through exhausted mixed-bed columns for a total of 300 minutes in three setups: NaOH/NaCl only, 150 minutes of H_2SO_4 followed by 150 minutes of NaOH/NaCl, and 150 minutes of NaOH/NaCl followed by 150 minutes of H_2SO_4.

Effects of operating and design parameters on phosphorus adsorption and elution have been well-characterized in previous studies. For example, phosphate adsorption with hybrid anion exchange resins such as LayneRT has been accurately modeled using a Freundlich isotherm and pseudo-second-order kinetic model;[16] batch adsorption densities have also been determined for influent streams with varying phosphate concentrations.[5] Regeneration of LayneRT has been optimized to 3.5 bed volumes with 2% NaOH/2% NaCl solution.[29] Compared to phosphate, effects of operating and design parameters on cation exchange columns for urine treatment are not well understood and were investigated through additional experiments in this study.

2.3 Operating Conditions and Adsorption

Effects of flow rate, influent concentration, and intermittent operation on nitrogen and potassium recovery were investigated through continuous adsorption experiments with synthetic urine and

198 Dowex Mac 3. Synthetic urine was used because of its constant composition (Table S2-S3),
199 whereas real urine composition varies among individuals, times, and regions.[30] Based on
200 potential variations in ammonia concentration in real urine, three dilutions of synthetic urine
201 were used: 8000 (undiluted), 5700, and 3600 mg N L^{-1}. 3600 mg N L^{-1} was indicative of
202 ammonia levels after dilution in NoMix source-separating flush toilets[31] and 5700 mg N L^{-1} was
203 chosen as an intermediate concentration. 4.5 mL min^{-1} was the estimated average urine
204 production rate for a five-person household; this flow rate was halved (2.2 mL min^{-1}) to better
205 represent U.S. conditions (2.5 people $household^{-1}$),[32] and doubled (10 mL min^{-1}) to simulate
206 conditions in which the urine could be collected and then pumped faster than the average
207 generation rate. Each flow rate and concentration condition was conducted in triplicate. Flow
208 rate variations were all conducted with ~1.6 L of undiluted synthetic urine and concentration
209 experiments were performed at constant flow rate (4.5 mL min^{-1} for 6 hours).
210
211 Intermittent flow was explored because it is more realistic than continuous operation, as toilet
212 use is intermittent. Intermittently run column experiments can also be used to confirm the rate-
213 limiting step of adsorption (e.g., external diffusion, intraparticle diffusion, surface reaction).[33]
214 External diffusion refers to transport of the adsorbate from bulk solution to the adsorbent surface,
215 intraparticle diffusion describes transport through the macropores, and the surface reaction is the
216 exchange of ions at adsorption sites.[34] Triplicate experiments were performed with synthetic
217 urine in which pumping (4.5 mL min^{-1}) was stopped for 24 hours after 1, 2, 3, and 5 hours of
218 cumulative operation.
219

For all column adsorption experiments, adsorption densities were calculated using numerical integration of breakthrough curves (Section S1.1, Equations S1-S2). All adsorption experiments were conducted without recirculation of synthetic urine.

2.4 Operating Conditions and Regeneration

Sulfuric acid was previously shown to achieve high recovery efficiency of ammonium from Dowex Mac 3 resin; specifically, 0.122 M H_2SO_4 (0.244 N H_2SO_4) pumped for 2.5 hours at 22.5 mL min^{-1} resulted in >99% nitrogen recovery efficiency.[10] To inform process optimization, we investigated the effects of eluent flow rates, eluent concentrations, and eluent species on regeneration performance metrics.

We expected low flow rates and high sulfuric acid concentrations to lead to high concentrations of ammonium sulfate eluent. Thus, experiments with 0.5, 1, 3, and 6 M H_2SO_4 were conducted at 2 and 4.5 mL min^{-1} using exhausted resin from synthetic urine adsorption. Next, to determine the effects of operating conditions on regeneration performance metrics, sulfuric acid flow rate and concentration were varied independently and by the same factors (22.5, 10, and 2.25 lower) from the previously established operating parameters that led to 99% nitrogen recovery (0.122 M/0.244 N H_2SO_4 at 22.5 mL min^{-1}).[10] To compare process performance for different regenerants that might reduce life-cycle impacts, columns were eluted with equinormal (0.244 N) H_2SO_4, HNO_3, HCl, and NaCl. Nanopure water and tap water were also used as regenerants to determine the extent to which adsorbed ammonia would desorb during resin exposure to water.

Experimental conditions were compared in terms of ammonium concentration in the fertilizer product, recovery efficiency, bed volumes to 90% elution, and stoichiometric efficiency. Recovery efficiency (Equations S1, S3) and produced ammonium concentration (Equation S7) were calculated by numerical integration. The number of bed volumes to 90% elution was calculated based on cumulative and total area under the elution curve (Equation S4). Stoichiometric efficiency (η_{stoich}) was defined as the proportion of supplied protons (based on commonly available stock concentrations, Table S4) that displaced an ammonium ion on Dowex Mac 3 (Equation 1).

$$\eta_{stoich} = \frac{q * W}{Q * t_{elution} * N * C_{regen}} \; x \; 100\% \qquad (1)$$

In Equation 1, q is adsorption density (mmol N g resin^{-1}= meq g resin^{-1}), W is resin mass (g resin), Q is flow rate (mL regenerant solution min^{-1}), $t_{elution}$ is time to 90% elution (min, to 90% of total amount eluted), N is normality of regenerant (meq mmol regenerant^{-1}), and C_{regen} is concentration of regenerant (mmol regenerant L regenerant solution^{-1}). Note that as defined, the stoichiometric efficiency is expected to be less than 100% due to the elution of other cations besides ammonium. This definition was chosen because our primary interest was maximizing nitrogen recovery. An alternative definition could account for elution of all cations.

2.5 Trace organic contaminants

A suite of 10 trace organic compounds, including antibiotics, antivirals, and beta blockers, was added to real urine before adsorption (Table S5). Compounds were measured in homogenized samples from multiple volunteers according to CPHS protocol 2016-10-9284. Trace organic compounds were quantified with an Agilent 1200 series HPLC (high-performance liquid chromatography) system followed by an Agilent 6460 mass spectrometer (triple quadrupole

tandem MS), according to previously published methods for wastewater.[35] To determine the fate of urine-relevant TrOCs during ion exchange, concentrations were measured in effluent samples during adsorption with real urine (4.5 mL min^{-1}) and regeneration with 0.122 M sulfuric acid (22.5 mL min^{-1}). Adsorption experiments were run until breakthrough was observed for all compounds (C_{out}/C_{in} >0.85). Based on compound detection limits, the lowest detectable recovery efficiency was 2.8%.

2.6 Chemical Analysis

Ion concentrations (NH_4^+, Na^+, K^+, Li^+, Mg^{2+}, Ca^{2+} and SO_4^{2-}, PO_4^{3-}, Cl^-, NO_2^-, NO_3^-, F^-, $C_2H_3O_2^-$, Br^-) were measured via ion chromatography using a Dionex chromatograph (IonPac CS12 column for cations, IonPac AS23 column for anions), as reported previously.[10] Samples were acidified to measure total ammonia nitrogen (TAN) as NH_4^+. pH was measured with a pH probe and meter (MP220, Mettler Toledo, Columbus, OH).

2.7 Modeling Breakthrough Curves

For every breakthrough curve generated, adsorption density was calculated by numerically integrating breakthrough curves and dividing by adsorbent mass (Equation S2). Breakthrough curves were compared using a two-parameter model that includes bed volumes to 50% breakthrough and slope of the breakthrough curve (Equation 2).[34]

$$\ln\left(\frac{\frac{C_t}{C_0}}{1-\frac{C_t}{C_0}}\right) = k'(b-\beta) \qquad (2)$$

In this model, C_t is concentration at time t, C_0 is initial concentration, and b is the number of bed volumes at time t. The two model parameters are k', the slope of the breakthrough curve, and β, the number of bed volumes to 50% breakthrough (C_t/C_0=0.5). The original model was adapted

from breakthrough curves that related absolute concentration and time to breakthrough curves in this study that related relative concentration and bed volumes.

2.8 Statistical Analysis

One-way ANOVA and paired t-tests were used to compare calculated adsorption densities and breakthrough model parameters for adsorption breakthrough curves for varying flow rate, influent concentration, and intermittency conditions. A two-tailed significance level of 1% ($p<0.01$) was used. Parameters (slope k' and bed volumes to 50% breakthrough β) for ammonium breakthrough curves for different combined nitrogen and phosphorus recovery schemes were also compared using one-way ANOVA and paired t-tests.

3. RESULTS AND DISCUSSION

3.1 Combined nitrogen and phosphorus recovery

3.1.1 Phosphorus Recovery

Phosphate was completely removed from hydrolyzed urine during struvite precipitation (Figure S1a). Based on the stoichiometry of nitrogen and phosphorus in struvite ($MgNH_4PO_4 \cdot 6H_2O$), concentrations of both species were expected to decrease by the same amount (25.9 mM P removed from urine). However, ammonium concentrations only decreased by 84% of the phosphate decrease (Figure S1b), indicating precipitation of phosphate minerals with cations other than ammonium (e.g., hydroxyapatite, $Ca_5(PO_4)_3OH$; potassium struvite formation was likely minimal as the decrease in dissolved potassium concentration was within experimental error).

Phosphate breakthrough curves for all three treatment trains are shown in Figure 1a. For struvite, phosphate was not detected after precipitation due to complete recovery with $MgCl_2$. Although slopes of the mixed-bed and in-series breakthrough curves did not differ significantly, the steeper slope of the in-series curve signaled faster adsorption kinetics (Table S6). Bed volumes to 50% breakthrough were significantly different (7.7 for mixed bed, 10.6 for in series), indicating a reduction in number of available phosphate adsorption sites or slower rate of filling them due to the presence of Dowex Mac 3. Phosphate adsorption densities for mixed-bed and in-series columns were 0.53 and 0.50 mmol g resin^{-1}, respectively, and were not significantly different (Table S6); both were higher than predicted based on expected adsorption densities from a Freundlich isotherm in hydrolyzed urine (0.255 mmol P g resin^{-1}, Equations S5-S6).[16]

3.1.2 Nitrogen Recovery

Nitrogen breakthrough curves for struvite supernatant fed to cation exchange, and urine fed to mixed-bed columns, separate columns, and cation exchange alone are presented in Figure 1b. Although struvite supernatant was characterized by more bed volumes to breakthrough and the lowest slope, the lack of statistically significant differences for number of bed volumes to 50% breakthrough and slope for all setups indicated similar ammonium adsorption rates (Table S7). Thus, the presence of LayneRT before cation exchange (in series) and in the same column as Dowex Mac 3 (mixed bed) did not significantly affect kinetics of ammonium adsorption. Ammonium breakthrough was observed latest (largest β) for struvite supernatant due to the removal of approximately 9% of ammonium during struvite precipitation and lower influent urine ammonium concentrations. Similarly, adsorption density for struvite supernatant was lower than all other setups, although only significantly lower than the mixed-bed column (Table S7).

335

336 *3.1.3 Potassium Recovery*

337 The molar adsorption density for potassium in synthetic urine (0.3-0.4 mmol K g resin^{-1}) was
338 more than ten times lower than the nitrogen adsorption density (4.23 mmol N g resin^{-1}). Both the
339 tenfold lower concentration of potassium in urine and the selectivity of Dowex Mac 3 for NH_4^+
340 contributed to low potassium adsorption. Potassium also began to break through the column
341 ($C_{out}/C_{in}>0$) at fewer bed volumes than nitrogen (Figure S2). Thus, to achieve higher potassium
342 recovery, it should be removed in a separate column from nitrogen or with an adsorbent other
343 than Dowex Mac 3. Bed volumes to 50% elution, slopes of breakthrough curves, and adsorption
344 densities did not differ significantly between setups, indicating that potassium adsorption was not
345 affected by phosphate recovery (Table S8). Potassium has not been a priority for nutrient
346 recovery because it has not been shown to contribute to eutrophication, it is less abundant in
347 urine than nitrogen, and it has a lower specific value than phosphorus (1.5 USD kg P^{-1}, 0.7-1
348 USD kg K^{-1});[36] thus potassium recovery was not optimized in this study. Future work could
349 optimize potassium recovery by potassium struvite precipitation or by cation exchange after
350 nitrogen recovery to enhance the value of combined nutrient fertilizers derived from urine.

351

352 *3.1.4 Considerations for implementation*

353 Molar nitrogen adsorption densities were up to an order of magnitude higher than phosphorus
354 adsorption densities due to the lower adsorption capacity of LayneRT (phosphate) compared to
355 Dowex Mac 3 (ammonium). Accounting for differences in adsorption density and concentration
356 in urine, the treatment of 1 L of urine would require 106 g LayneRT and 50 g Dowex Mac 3.
357 Thus, mixed-bed columns should have roughly twice as much LayneRT as Dowex Mac 3, and

for separate columns the cation exchange column could contain half the resin mass as the anion exchange column.

While separate regenerants can be used for each resin type for columns in series, regeneration of a mixed-bed column exposes both anion and cation exchange resins to any regenerant used. For mixed-bed regeneration, ammonium recovery efficiencies were higher than phosphate recovery efficiencies for all regenerants tested (50-60% for N and 20-30% for P, Figure S3). Desorption of ammonium occurred faster than phosphate desorption due to the more tightly bound Lewis acid-base interactions between phosphate and the anion exchange resin.[22] Further decreasing flow rate (below 2 mL min^{-1}, thus increasing hydraulic residence time) could potentially enhance phosphate recovery efficiency. 2% NaOH/2% NaCl exhibited the highest recovery efficiencies for both phosphorus and nitrogen (Figure S3). Compared to NaOH/NaCl, eluting with sulfuric acid first halved the phosphorus recovery efficiency, and eluting with sodium chloride/hydroxide first reduced ammonium recovery efficiency by 10% (Figure S3). Thus, exposing LayneRT to a pH far below its operating range (5.5-8.5) negatively affected phosphate desorption more than sodium affected ammonium desorption.

Based on our results, operating cation and anion columns separately (rather than in a mixed bed) appears more promising for maximizing the recovery efficiency of nitrogen, potassium, and phosphorus. In addition, recovering the nutrients separately would allow them to be recombined in different ratios to produce tailored fertilizers. Also, phosphorus recovery could occur through struvite precipitation (stored urine) or anion exchange (fresh or stored urine). Recovering phosphate via anion exchange in fresh urine would reduce the precipitation of phosphate

minerals such as struvite and hydroxyapatite because of low ammonia concentrations and the lower pH of fresh urine (6 vs. 9 in stored urine).[5] Urea hydrolysis could be accelerated by adding urease enzyme or optimizing conditions for microbial hydrolysis (e.g., fixed biofilm column, increasing temperature). For example, phosphorus precipitation from fresh urine, urea hydrolysis in a fixed biofilm column, and ammonium and potassium adsorption in separate cation exchange columns operated in series could be an effective treatment scheme.

3.2 Effects of operating conditions on adsorption

The number of bed volumes to breakthrough varied inversely with total ammonia concentration in influent synthetic urine and was significantly different for each concentration (Figure 2a). This trend was expected given a fixed number of sites available per gram of resin, which were occupied in fewer bed volumes when more ammonium ions were present (higher concentration). The slope of the breakthrough curves was not significantly different for varying concentrations. Adsorption densities did not differ significantly (Figure S4), which was expected given that this range of the adsorption isotherm is relatively flat.[10]

Variations in flow rate within the range tested did not have a significant impact on bed volumes to breakthrough nor slope of the breakthrough curve (Figure 2b). Adsorption densities for varying flow rates were not significantly different (Figure 2c). Because breakthrough curve slope was not affected by increasing flow rate from 2.2 to 10 mL min^{-1} (and thus the rate at which ammonium is supplied), transport through the liquid film could be excluded as the rate-limiting step of the adsorption process within this range.[33]

Intermittent flow of urine led to similar adsorption density as continuous flow (no significant difference). After each 24-hr rest period, effluent ammonium concentrations decreased (Figure 2d). This decrease could have been due to microbial oxidation or sorption. Based on low NO_2^- and NO_3^- concentrations in the column effluent (below detection limit of 1 mg L^{-1}), additional ammonium adsorption was identified as the predominant mechanism. Gaseous products (e.g., N_2, NO, N_2O) could have been formed from microbial oxidation, but no bubbles were observed despite N_2, NO, and N_2O being water-insoluble gases ($K_H \leq 2.5 \times 10^{-2}$ M atm^{-1},[37] Table S9). Ammonia adsorption during quiescence demonstrated that intraparticle diffusion (i.e. transport through resin macropores) was likely the rate-limiting step of ammonia removal via ion exchange.[33] Ammonia concentrations no longer decreased once the resin was exhausted (i.e., between day 4 and day 5).

For potassium adsorption, the only significant differences were between the number of bed volumes to 50% breakthrough for the most dilute influent concentration and the other concentrations tested (Figure S2). Adsorption densities were not significantly different and no clear trend was observed (Figure S6). Potassium emerged from the column in fewer bed volumes than ammonium for all conditions tested.

3.3 Effects of operating conditions on regeneration

In addition to having a high recovery of the target nutrient(s), an optimal regenerant would have few bed volumes to elution and a high stoichiometric efficiency. The last parameter minimizes the volume of regenerant required for elution, which is important because our previous analysis identified that the acid regenerant dominated the life-cycle costs, embedded energy, and

427 greenhouse gas emissions of the entire process.[28] Also, for ion exchange to be a viable process
428 for nutrient recovery from urine, nutrients in the final product must be significantly more
429 concentrated than in the original urine.
430
431 The impact of different operating conditions on the elution step was investigated using
432 ammonium as the target nutrient. The first objective was to determine if up-concentration could
433 be achieved, i.e., was the nitrogen concentration in the ammonium sulfate eluent higher than in
434 the influent urine. We estimated that the theoretical minimum number of bed volumes required
435 to up-concentrate ammonium from urine was 8, assuming the urine contained 5 g N L^{-1}
436 (Equation S9). Experimentally, we achieved up-concentration using 0.5 to 6 M H_2SO_4 (Table 1).
437 A more concentrated product was achieved with stronger acid, with a final ammonium sulfate
438 product containing 22 g N L^{-1}, which is 25% of common $(NH_4)_2SO_4$ liquid fertilizers available
439 on the market (Equations S7-S8).[38,39] Instantaneous ammonium concentrations were as high as
440 60 g N L^{-1} (Figure S7a). Bed volumes to elution were minimized to 2.78 bed volumes using 6 M
441 H_2SO_4, whereas 5.15 bed volumes were required when 0.5 M H_2SO_4 was used. However, the
442 stoichiometric efficiency was lower for the higher concentration eluent: 19% compared to 83.5%
443 for 6 and 0.5 M H_2SO_4, respectively (Table 1). Thus, there was a trade-off between up-
444 concentrating the nitrogen and using the acid eluent efficiently.
445
446 Increasing the regeneration flowrate from 2 to 4.5 mL min^{-1} did not appear to impact elution
447 performance (Figure S7b). For all four H_2SO_4 concentrations, most regeneration parameters
448 (e.g., recovery efficiency, final ammonium concentration) differed by less than 15% at 2 and 4.5
449 mL min^{-1} (Table 1, Table S10). Similar concentration trends were observed at both flow rates, as

higher H_2SO_4 concentrations led to lower bed volumes to elution, lower stoichiometric efficiencies, and higher final ammonium concentrations. Nonetheless, we wanted to explore the impacts of flow rate and concentration of acid regeneration over a wider range of conditions. Based on preliminary experiments, repeatable samples could not be collected quickly enough to generate reliable elution curves at high sulfuric acid concentrations and higher flow rates (>4.5 mL min^{-1}). Thus, we compared elution at flow rates and concentrations that allowed us to explore these variables but were not effective for up-concentration.

Elution curves for varying flow rate and sulfuric acid concentration are shown in Figure S5. Stoichiometric efficiency varied inversely with flow rate and sulfuric acid concentration (Figure 3). Nitrogen recovery efficiency was consistently above 90%, with the exception of the 5.42 mM sulfuric acid, the lowest concentration tested (Figure S8). Although increasing flow rate did not have a significant effect on bed volumes to 90% elution, increasing concentration drastically reduced bed volumes to elution (Figure 3a). Regenerant concentration had a larger effect (higher absolute value of slope) than flow rate on stoichiometric efficiency and bed volumes required for both nitrogen (Figure 3) and potassium (Figure S9). Based on these results, proton activity was the predominant operating parameter influencing the volume of acid required for elution. The lack of effect from flow rate on bed volumes to elution indicated that proton loading rates for the flow rates tested were sufficiently high to desorb ammonium. For potassium, most recovery efficiencies were above 90% (Figure S10).

While up-concentration is desirable, more acid was required for concentrating ammonium during elution, demonstrating that it was not possible to maximize both product concentration and

stoichiometric efficiency. To overcome this limitation, future work could explore re-using the ammonium sulfate eluent for multiple elutions to produce more concentrated product and increase the stoichiometric efficiency. Alternatively, elution could be optimized for stoichiometric efficiency, and a separate step, such as reverse osmosis, could be added to concentrate the eluent.

3.4 Comparing regenerants

Bed volumes to 90% elution, stoichiometric efficiency, and nitrogen recovery efficiency for equinormal (0.244 N) HNO_3, HCl, NaCl, and H_2SO_4 are compared in Table 2 (elution curves in Figure S11). Of the regenerants tested, sulfuric acid exhibited the lowest number of bed volumes to elution and stoichiometric efficiency, indicating the most efficient use of regenerant. The only significant differences between performance metrics for different regenerants were the nitrogen recovery efficiency of NaCl (77%) with all other regenerants (all approximately 100%). NaCl had a lower nitrogen recovery efficiency because of the lower affinity of Dowex Mac 3 for sodium ions compared to protons and ammonium.[10] This low performance of NaCl regeneration may potentially be mitigated by using more concentrated NaCl regenerants. With NaCl, the Na^+ sorbed during column regeneration would desorb during subsequent urine treatment, increasing the salinity of the urine effluent. If this stream is disposed to the sewer, it could be a disadvantage for treatment plants that discharge to inland freshwater or if the water is reused; for ocean discharge, the additional salinity is likely not an issue.

For potassium recovery with Dowex Mac 3, no significant differences in elution metrics were observed. At most 8% of protons contributed to potassium desorption for all regenerants, which

was expected given the tenfold lower adsorption density of potassium compared to ammonium. Similar to nitrogen results, all three acid regenerants exhibited potassium recovery efficiencies of at least 100% while NaCl was only 87%; sulfuric acid had the lowest number of bed volumes to 90% potassium elution (Table S11).

To evaluate the potential for desorption if the column is exposed to water, nanopure water and tap water were used as regenerants on ammonium-loaded Dowex Mac 3 resin. Based on elution curves (Figure S12), only 6.9% (nanopure) and 8.9% (tap) of sorbed ammonium was desorbed during 2.7 L of water flow. The low proton concentration in these waters can explain the unfavorable desorption of ammonium. Low levels of elution with water indicate that desorption of ammonium due to exposure to very dilute urine streams, flush water, or water used for cleaning is not a major impediment.

3.5 Fate of indicator trace organics

Trace organics could adsorb to Dowex Mac 3 via electrostatic or van der Waals interactions. As expected, only trace organic contaminants that were positively charged at stored urine pH (~9.1) were adsorbed (Figure 4a), indicating electrostatic interactions as the primary mechanism. Neutral and negatively charged compounds of similar size to adsorbed compounds were not adsorbed to Dowex Mac 3, including sulfamethoxazole, acetaminophen, acyclovir, and emitricitabine. Adsorbed compounds were identified as positively charged based on comparing stored urine pH to published pK_a values (Table S5), with two exceptions: abacavir and trimethroprim (Figure 4a). Although abacavir has a published pK_a of 5.01, it is regarded as a monoacidic base because of delocalized positive charge in the heterocycle.[40] Similarly,

519 trimethroprim has a pK_a of 7.4, which would indicate neutral charge at pH 9 in stored urine.
520 However, trimethroprim has been particularly well-removed by synthetic macroprous resins and
521 zeolites;[41] it has also been suggested to be positively charged when bound to enzymes like
522 dihydrofolate reductases.[42] These enzymes are required for production of purines and some
523 amino acids, and are thus ubiquitous in bacterial cells present in stored urine (~5 x 10^8 cells mL^{-1}).[3]
524
525
526 TrOC adsorption onto anion exchange resins has been measured and modeled for several non-
527 steroidal anti-inflammatory drugs (e.g., diclofenac, naproxen).[27] Acetaminophen (also called
528 paracetamol) was the only compound also monitored in this study, and did not appreciably
529 adsorb to anion nor cation exchange resins due to only 40% being negatively ionized (60%
530 neutral) at pH 9. For anion exchange reins, electrostatic interactions were responsible for TrOC
531 adsorption densities while selectivity was a function of hydrophobicity.[27] Based on only
532 positively charged organic compounds adsorbing to Dowex Mac 3, adsorption density and thus
533 removal efficiency during adsorption were functions of electrostatic interactions. Given the
534 similar polymeric backbones of anion and cation exchange resins, selectivity is also expected to
535 be a function of hydrophobicity and van der Waals interactions for cation exchange resins. In
536 future work similar suites of prevalent trace organic compounds could be applied to both resin
537 types.
538
539 Elution suited for nitrogen recovery was used with TrOC-loaded resin to determine TrOC
540 concentrations in produced ammonium sulfate and recovery efficiencies for trace organics. Only
541 beta blockers (atenolol and metoprolol) were eluted (Figure 4b), and at less than 10%

efficiencies. This finding indicates that the majority of atenolol and metoprolol, as well as compounds that were adsorbed but not eluted (carbamazepine, zidovudine, abacavir, and trimethroprim), will continue to accumulate on Dowex Mac 3 over multiple adsorption-regeneration cycles. Atenolol (0.046 ± 0.013 μg L^{-1}) and metoprolol (0.077 ± 0.028 μg L^{-1}) were also the only compounds at detectable levels in the ammonium sulfate product.

Many pharmaceuticals present in urine are contaminants of emerging concern that should be treated before discharge to avoid harming aquatic organisms. Based on many TrOCs passing through cation exchange columns, pre-or post-treatment for TrOC removal in urine will be required. For the compounds that accumulate on Dowex Mac 3, regeneration may be required and has been demonstrated for anion exchange resins with 5% (m/m) NaCl with equal volumes of water and methanol.[27] Atenolol and metoprolol in the ammonium sulfate product should also be monitored for environmental impacts. When biosolids containing atenolol were applied to corn, carrot, and potato crops, atenolol was detected in the 0.5-1 ng L^{-1} range in the plants, which was not considered significant uptake.[43] Metoprolol may behave similarly, but has not been measured during field trials. While these data indicate that urine-derived ammonium sulfate concentrate does not contain biologically significant pharmaceutical levels, future work can more robustly answer this question for additional compounds to ensure urine-derived fertilizers do not lead to additional uptake of pharmaceuticals by crops.

4. Conclusions

In this study, the effects of operating parameters of adsorption and regeneration on system performance were investigated for nutrient recovery via ion exchange. Based on previous life-cycle analysis that indicated sulfuric acid manufacturing contributes significantly to energy use

566 and greenhouse gas emissions,[28] efficacies of alternative regenerants were compared. Removal
567 of trace organics during cation exchange was determined, and treatment schemes for nitrogen
568 and phosphorus recovery were compared. Overall, these findings contribute to an improved
569 understanding of continuous-flow nitrogen recovery via ion exchange. The major implications of
570 this work for implementation were:

571 • Several configurations for recovery of phosphorus, nitrogen, and potassium were
572 identified, either by operating anion and cation exchange in series or by integrating
573 struvite precipitation with cation exchange.
574 • Ammonium recovery from urine can be performed intermittently and regenerated
575 periodically to produce ammonium sulfate concentrate.
576 • Acidic regenerants performed better than sodium chloride and avoid brine generation.
577 • Trace organics that are positively charged at pH 9 were co-adsorbed with ammonium.
578 Adsorbed compounds were not substantially eluted into the ammonium sulfate product,
579 but may accumulate on resin over several adsorption-regeneration cycles.

580 Based on these conclusions, the primary barriers to adoption relate to implementation and can be
581 better understood at pilot scale. To advance ion exchange-based nutrient recovery from urine,
582 future work could more comprehensively analyze the fate of additional trace organic compounds
583 and optimize nitrogen recovery in terms of product concentration and efficient regenerant use.
584 Based on a vision for selective nutrient recovery and production of customized fertilizers of any
585 desired NPK (nitrogen: phosphorus: potassium) ratio, additional adsorbents for phosphate and
586 potassium recovery could be further explored and integrated into a complete treatment train for
587 nutrient recovery from source-separated urine.
588

589 **ASSOCIATED CONTENT**

590 The Supporting Information (SI) contains equations for breakthrough curve parameters,
591 composition of synthetic urine and properties of trace organic contaminants, and adsorption and
592 elution curves. This information is available free of charge via the Internet.

593

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597 **Notes**

598 The authors declare no competing financial interests.

599

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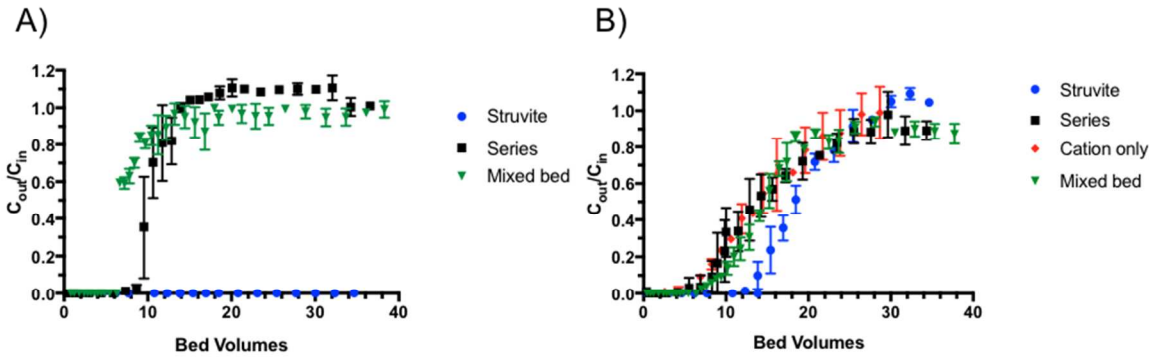
674 **FIGURES**

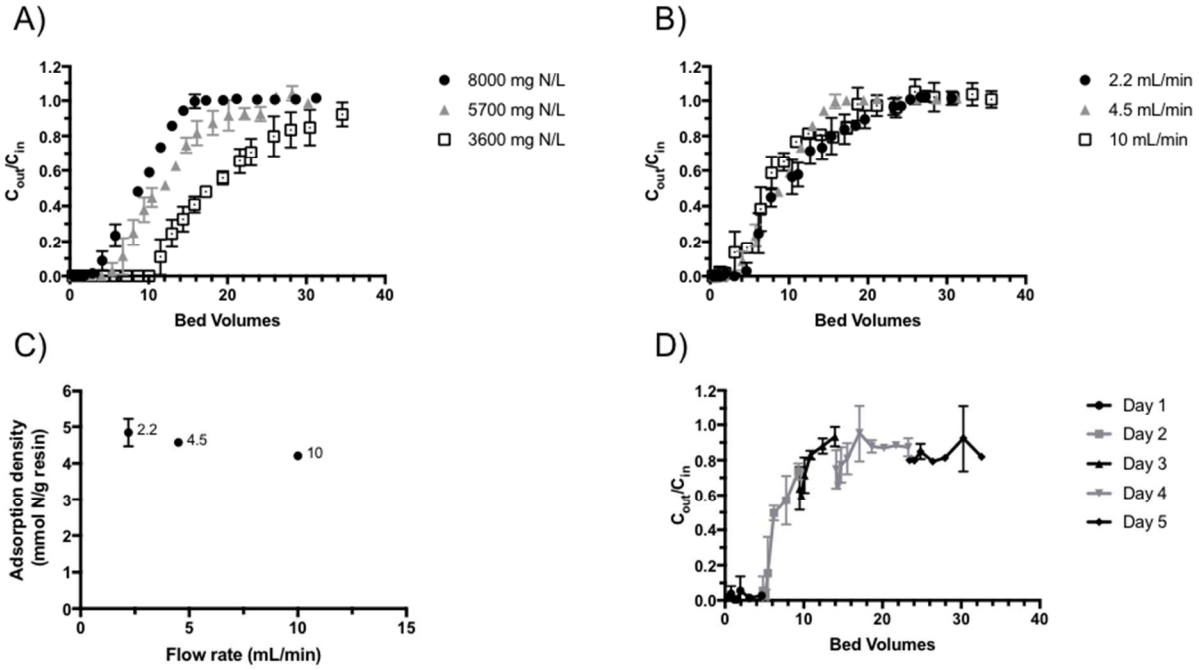


675

676 **Figure 1.** Breakthrough curves for varying treatment trains for (a) phosphorus as phosphate and

677 (b) nitrogen as ammonium.

678



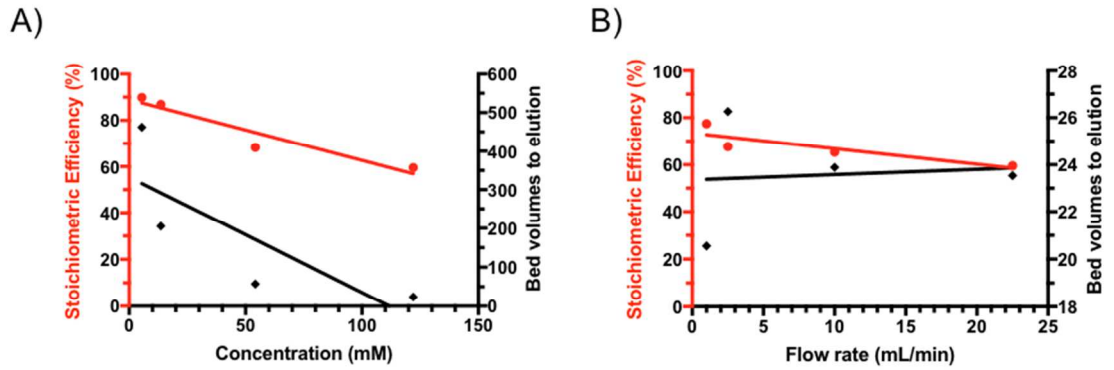
679

680 **Figure 2.** Ammonium breakthrough curves with synthetic urine influent for (a) varying influent

681 TAN concentration and (b) varying flow rate. Panel (c) shows adsorption densities for varying

682 flow rate with undiluted synthetic urine (8000 mg N L^{-1}), and point labels are flow rates. Panel

683 (d) shows ammonium breakthrough for intermittent operation. Error bars represent ± one
684 standard deviation for experimental triplicates. Error bars not shown are smaller than symbol.

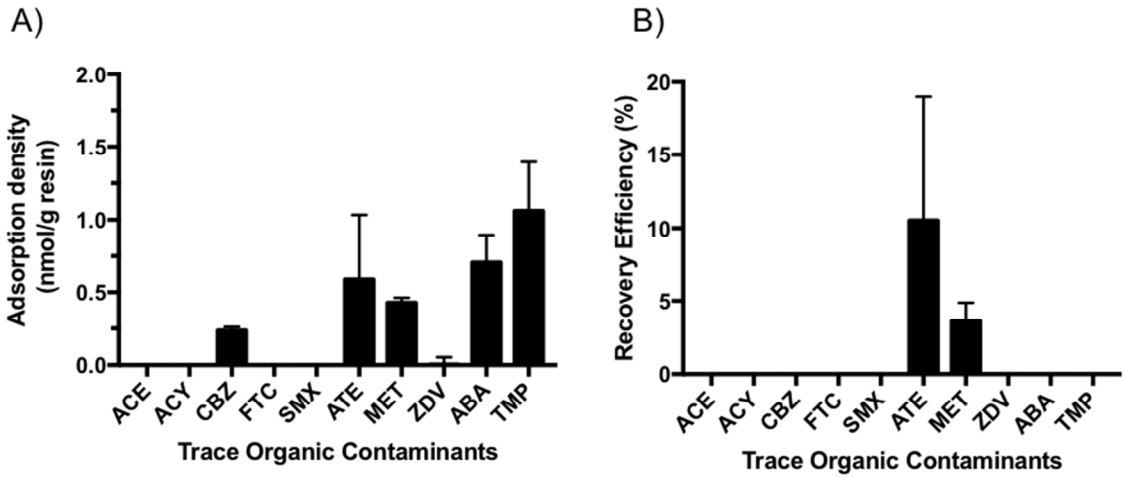


685

686 **Figure 3.** Sulfuric acid use efficiency compared to stoichiometric exchange for ammonium
687 elution and column regeneration with (a) varying concentration (flow rate constant at 22.5 mL
688 min^{-1}) and (b) varying flow rate (concentration constant at 122 mM H_2SO_4). Linear regression
689 lines show slope of each correlation. Resin was exhausted during adsorption with synthetic urine.

690

691



692

693 **Figure 4.** (a) Adsorption density and (b) recovery efficiency of trace organic contaminants with
694 cation exchange resin Dowex Mac 3. Compound abbreviations are in Table S5.

TABLES

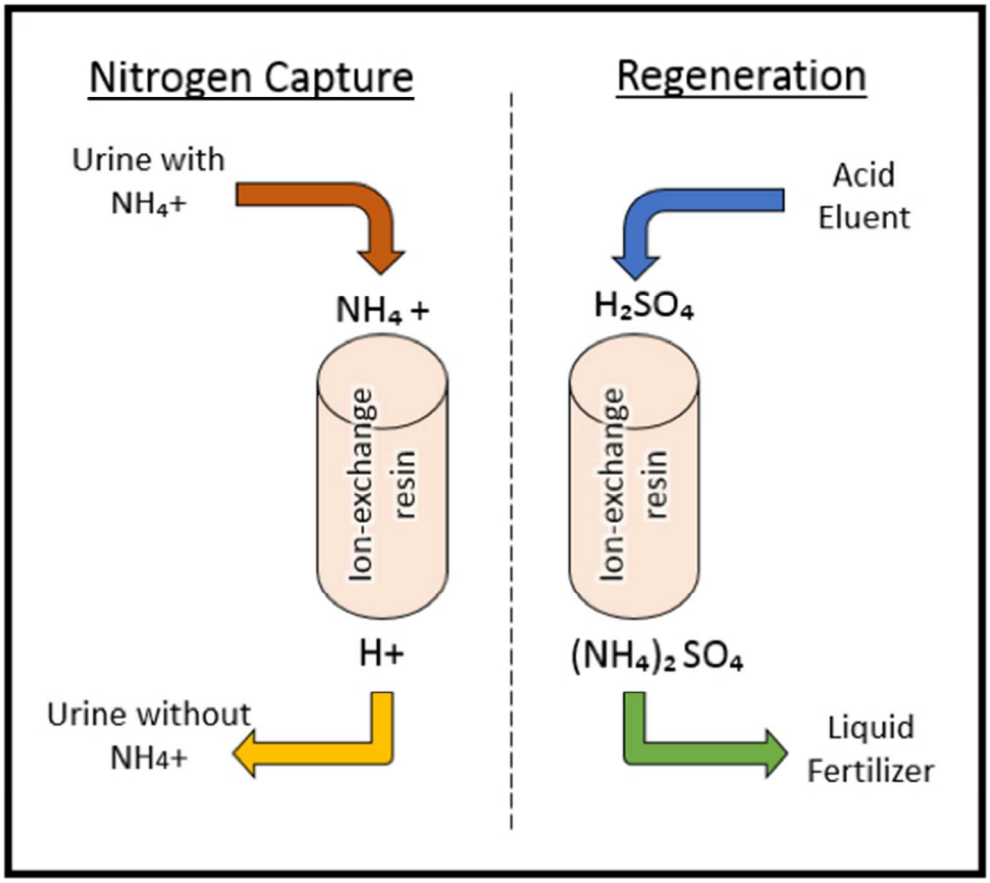
Table 1. Ammonium recovery efficiencies, stoichiometric efficiencies, final eluent concentrations, and bed volumes to 90% elution for elution experiments at high concentration and 2 mL min^{-1}. Resin was exhausted during adsorption with synthetic urine. TAN is total ammonia nitrogen.

H_2SO_4 Concentration (M)	Bed volumes to 90% elution	Stoichiometric Efficiency (%)	Recovery Efficiency (%)	Final Eluent TAN (g N L^{-1})
0.5	5.15	83.5	90.7	7.87
1	5.06	54.4	88.4	7.21
3	3.02	33.3	81.4	22.3
6	2.78	19.1	101	22.2

Table 2. Ammonium recovery efficiencies, stoichiometric efficiencies, and bed volumes to 90% elution for triplicate elution experiments with various regenerants. Resin was exhausted during adsorption with synthetic urine. Error values denote standard error of the mean (SEM).

	Bed volumes to 90% elution	Stoichiometric Efficiency (%)	Recovery Efficiency (%)
HNO_3	21.9 ± 1.76	95.3 ± 2.4	104 ± 1.8
HCl	23.2 ± 0.87	101 ± 3.4	102 ± 4.2
NaCl	28.9 ± 2.81	85.9 ± 10.7	77.4 ± 5.5
H_2SO_4	20.0 ± 2.19	107 ± 16.8	99.3 ± 0.3*

*experimental duplicate


Nitrogen Capture
Regeneration
Urine with
NH4+
NH4 +
Ion-exchange resin
H+
Urine without
NH4+
Acid
Eluent
H2SO4
Ion-exchange resin
(NH4)2 SO4
Liquid
Fertilizer