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Comparing ion exchange adsorbents for nitrogen recovery from source-separated urine

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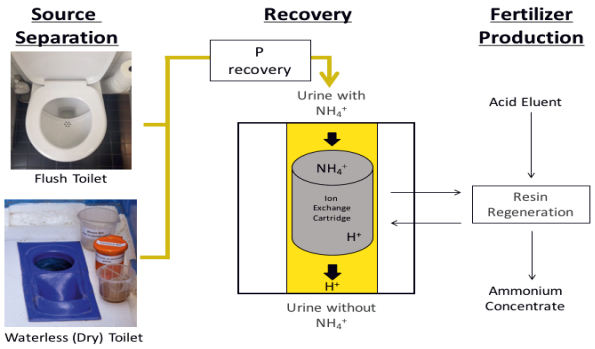

ABSTRACT

Separate collection of urine, which is only 1% of wastewater volume but contains the majority of nitrogen humans excrete, can potentially reduce the costs and energy input of wastewater treatment and facilitate recovery of nitrogen for beneficial use. Ion exchange was investigated for recovery of nitrogen as ammonium from urine for use as a fertilizer or disinfectant. Cation adsorption curves for four adsorbents (clinoptilolite, biochar, Dowex 50, and Dowex Mac 3) were compared in pure salt solutions, synthetic urine, and real stored urine. Competition from sodium and potassium present in synthetic and real urine did not significantly decrease ammonium adsorption for any of the adsorbents. Dowex 50 and Dowex Mac 3 showed nearly 100% regeneration efficiencies. Estimated ion exchange reactor volumes to capture the nitrogen for one week from a four-person household were lowest for Dowex Mac 3 (5 L) and highest for biochar (19 L). Although Dowex Mac 3 had the highest adsorption capacity, material costs ($/g N removed) were lower for clinoptilolite and biochar because of their substantially lower unit cost.

1. INTRODUCTION

Source separation, in which urine and feces are separated at the toilet, has recently emerged as a potential alternative to conventional wastewater management, in which all wastewater is combined and treated together.[1] Separately collecting and treating distinct waste streams could allow for more optimal approaches to recover embedded resources,[2] and reduce energy and financial costs for wastewater treatment.[3,4] Conventional biological treatment removes nitrogen as dinitrogen gas (N_2); this process simply reverses energy-intensive fertilizer production via the Haber-Bosch process, from which most of the wastewater nitrogen was derived.[5] Recovering reduced nitrogen directly from wastewater closes the loop between fertilizer production and wastewater treatment more efficiently than using N_2 as an intermediate. Urine has emerged as a waste stream of increasing interest because it comprises only 1% of wastewater volume but contains the majority of excreted macronutrients.[1] Furthermore, nitrogen-based fertilizers and disinfectants could potentially be a revenue source;[6,7] this creation of valuable products distinguishes recovery from removal.

Source separation could potentially be integrated into existing centralized wastewater infrastructure to reduce nutrient loads on wastewater treatment plants.[8] For example, as San Francisco and Paris are facing potential large capital investments to remove nitrogen from wastewater to reduce eutrophication in receiving waters,[9,10] source separation and resource recovery technologies are being considered.[11] Source separation could also be used to reduce nitrogen loads from on-site sanitation due to failing septic systems,[4] and in urban areas that lack formal infrastructure, such as the decentralized approaches being pursued by Sanergy in low-income, high-density settlements in Nairobi, Kenya[12] and the Valorization of Urine Nutrients

(VUNA) project in Durban, South Africa.[13] To inform the choice between source separation/resource recovery and current wastewater management approaches, technologies that enable the new paradigm must be further developed and more rigorously characterized.

Ion exchange is a promising technology for nitrogen recovery from source-separated urine. During urine storage, urea is hydrolyzed to ammonium (NH_4^+),[14] which can adsorb onto materials with negatively charged sites. Although cation exchange has been studied for removing NH_4^+ from NH_4Cl solutions,[15] drinking water,[16] and landfill leachate[17] at concentrations less than 800 mg N/L, it has only been preliminarily documented for urine treatment, which has NH_4^+ concentrations of around 5000 mg N/L.[18] Multiple studies have examined sorption of phosphate and pharmaceuticals from synthetic urine by anion exchange resins.[19,20] Cation exchange adsorbents could also be used for potassium recovery. Suitable adsorbents can be selected and combined to remove the resources or pollutants of interest. As a physicochemical process, sorption may be more stable than biological nitrogen removal. Because the required adsorbent mass and reactor size are proportional to the mass of compound removed, sorption can be applied at varying scales. Sorption's selective, stable, and scalable nature make it a promising option for resource recovery from urine.[21]

To our knowledge, this investigation is the first to compare the feasibility of a diverse set of ion exchange adsorbents for cation recovery from source-separated urine. Four ion exchange adsorbents were tested: clinoptilolite, biochar, Dowex 50, and Dowex Mac 3. Clinoptilolite is extremely abundant, naturally-occurring, and has been documented for removing ammonium from drinking water,[22] wastewater,[22,23] and, preliminarily, source-separated urine.[24] Biochar is

already being used as a soil conditioner for nutrient and moisture retention and can be produced economically from a variety of feedstocks.[25,26] One such feedstock is feces, which could make possible a scheme in which feces-based biochar is used to recover ammonium from separately collected urine. Dowex 50 is a standard synthetic cation exchange resin, and Dowex Mac 3 is another synthetic cation resin with purported ammonium specificity,[27] suggesting it may be particularly suited to ammonium recovery from source-separated urine.

In this study, factors affecting ammonium adsorption were explored in solutions of increasing complexity: pure salt, synthetic urine, and real urine. Experiments were designed to measure two major determinants of feasibility: adsorption capacity and regeneration potential. Adsorption capacity describes how much nitrogen can be captured each sorption cycle per mass of adsorbent (before regeneration) and can be used to determine minimum reactor size. Regeneration potential influences adsorbent lifetime, and therefore how much urine the adsorbent can treat before replacement. The specific objectives of this study were to: (i) characterize adsorption in ideal solutions with respect to the Langmuir parameters maximum adsorption density, q_{max}, and affinity constant, K_{ads}; (ii) characterize adsorption isotherms in synthetic and real urine, including the effect of sodium and potassium competition on ammonium adsorption; (iii) determine adsorption capacity and regeneration efficiency in column experiments; and (iv) estimate adsorbent costs and reactor volume to preliminarily assess the feasibility of ion exchange for nitrogen recovery from source-separated urine.

2. MATERIALS AND METHODS

2.1 Description of Adsorbents

Four adsorbents were examined in this study: clinoptilolite (Multavita, Castle Valley, MT), biochar (Ithaca Institute, Ayent, Switzerland), Dowex 50 (Alfa Aesar, Ward Hill, MA), and Dowex Mac 3 (Sigma Aldrich, St. Louis, MO). Clinoptilolite is an aluminosilicate zeolite with negatively charged sites due to the isomorphic substitution of trivalent aluminum for tetravalent silicate groups. As the most abundant natural zeolite, it is isolated from naturally occurring mineral deposits in many countries, including Turkey, South Africa, Australia, China, and the United States.[22] Biochar is a carbon-rich product made by thermal decomposition of organic material under limited supply of oxygen and at a temperature greater than 700°C.[28] Within this definition, biochar varies extensively in form, feedstock, and processing method. The biochar used in this study was from wood husks (950°C for 2 hours, no pretreatment); similar biochars have carboxyl functional groups.[26] The adsorption sites of Dowex 50 and Dowex Mac 3 are sulfonic acid and carboxylic acid moieties, respectively. This difference in functional groups makes Dowex 50 effective over a wider pH range than Dowex Mac 3.[27,29] Both Dowex resins are available with protons initially adsorbed to functional sites. Dowex Mac 3 is marketed as an ammonium-specific cation exchange resin produced from a polyacrylic matrix and added carboxylate moieties.[27] For further information on adsorbents see Table S1.

2.2 Solution Types

To examine the factors and mechanisms affecting adsorption in urine, four solutions were used, ranging from ideal to real: (i) NH_4Cl without pH adjustment; (ii) NH_4Cl at pH 9; (iii) synthetic stored urine (pH ~ 9); and (iv) real stored urine (pH ~ 9). Because NH_4^+ is a weak acid (pK_a 9.25)[30], the pH of the 9000 mg N/L NH_4Cl solution without adjustment was 4.72. For ease of reference, we call these "pH 4 experiments." The effect of pH on ammonium adsorption was

elucidated by comparison with pH 9 NH_4Cl, which is closer to the pH of stored urine and the NH_4^+/NH_3 pK_a. Synthetic stored urine was used to observe the effect of competition on ammonium adsorption by other cations, such as Na^+ and K^+. We used an existing synthetic urine recipe based on real urine concentrations (Table S2).[31] Organic acids are the primary organic constituent of urine;[31] acetic acid is used in synthetic urine to represent organic acids. Finally, real source-separated urine from NoMix toilets and waterless urinals was used.[7] The real urine was from the men's collection tank of the Swiss Federal Institute of Aquatic Sciences and Technology's (Eawag) main building *Forum Chriesbach* (composition in Table S3). Given the extended storage time, urea was completely hydrolyzed to ammonia/ammonium and magnesium and calcium concentrations were negligible due to struvite and hydroxyapatite precipitation.[32] In addition to the four solution types above, NaCl and KCl solutions were also prepared without pH adjustment. These results served as inputs for competitive adsorption models to which synthetic urine results were compared. All experiments were conducted at room temperature (23 ± 2 °C) with nanopure water and analytical grade chemicals.

2.3 Batch Adsorption Experiments

Batch adsorption experiments were conducted by adding 0.015 g adsorbent to 1.5 mL of solution and continuously mixing for 24 hours to ensure equilibration (based on preliminary experiments). Samples were then centrifuged at 2000 rpm for five minutes to separate adsorbent and solution. Aliquots from the initial solution and the supernatant were analyzed for NH_4^+, Na^+, and K^+ concentrations via ion chromatography (Metrohm chromatagraph, IonPac CS12 column, 30 mM methanesulfonic acid eluent, 1.0 mL/min, 30 °C). A six-cation chloride calibration standard (LiCl, NaCl, NH_4Cl, KCl, $MgCl_2$, $CaCl_2$) was diluted 100, 50, 20, 10, and 6.25 times to

generate a calibration curve. A mass balance was used to calculate the final adsorption density (q_f) at equilibrium according to Equation 1:

$$V_L(C_0 - C_f) = W(q_f - q_0) \quad (1)$$

where V_L is solution volume (L), C_0 is initial concentration of adsorbate (mg NH_4^+-N, Na^+, or K^+/L), C_f is adsorbate concentration at equilibrium (mg NH_4^+-N, Na^+, or K^+/L), W is adsorbent mass (g), and q_0 is the initial adsorption density (mg NH_4^+-N, Na^+, or K^+/g adsorbent). To compare adsorption densities between cation species, molar mass was used to convert adsorption densities to mmol/g adsorbent.

For pH 4 experiments, 16 initial NH_4Cl solutions with ammonia concentrations varying from 25-9000 mg N/L were prepared without pH adjustment. For pH 9 experiments, NH_4OH was added to increase pH. For synthetic and real urine experiments, one master solution was made and diluted to 15 different concentrations to generate adsorption curves. Real urine was filtered (0.47 μm) to exclude precipitates that might have interfered with adsorption. Although initial pH differed for each dilution in a given adsorption curve, we refer collectively to each set of experiments by the pH of the most concentrated initial solution. For example, we refer collectively to samples prepared from the 9000 mg N/L NH_4Cl at pH 9 as "pH 9 experiments" although pH was less than 9 for many dilutions.

2.4 Continuous Adsorption Experiments

Upflow continuous adsorption experiments were performed in PVC columns (2.54-cm diameter, 16-cm length) packed with each adsorbent, sponges to retain media, and pretreated with 1 M borate buffer. Synthetic urine was pumped through each column at 4.5 mL/min for 6 hours, and

samples from the end of the column were collected every 20 minutes and analyzed for ammonium and chloride (used as a conservative tracer) via ion chromatography. Adsorption densities were calculated by numerically integrating breakthrough curves and dividing by adsorbent mass (Equation S6).

2.5 Continuous Regeneration Experiments

Regeneration experiments were similar to adsorption experiments, except with 0.1 M H_2SO_4 pumped at 22.5 mL/min for 2 hours and samples collected every 10 minutes. Regeneration efficiencies were calculated by dividing moles of ammonium eluted (integration of elution curve, Figure S1) by the moles adsorbed (Equation S7).

2.6 Modeling

To account for non-ideality of concentrated ionic solutions, PHREEQC software[33] was used to determine Pitzer activity coefficients based on the concentrations in each initial solution. Cation chromatography measures total ammonia concentrations. Ammonia/ammonium speciation was determined according to Equations 2-4 using measured values of pH and temperature:[34]

$$K_{NH_4^+|T_2} = K_{NH_4^+|T_1} x \exp\left[\frac{\Delta H_R}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \quad (2)$$

$$[NH_4^+] = \frac{N_{tot}}{1+\gamma_{NH_4^+} 10^{pH-pK_{NH_4^+}}} \quad (3)$$

$$\{NH_4^+\} = \gamma_{NH_4^+}[NH_4^+] \quad (4)$$

where $K_{NH_4^+}$ is the ammonium acid dissociation constant at 25 °C (9.25),[30] R is the universal gas constant, T is temperature, N_{TOT} is total ammonia concentration, [] denotes molar concentration, {} denotes chemical activity, and $\gamma_{NH_4^+}$ is the Pitzer activity coefficient for ammonia.

Adsorption curves were fit to the single-solute Langmuir model for each adsorbent (Equation 5, where n=1).[35] q_f is the adsorption density (mmol NH_4^+, Na^+, or K^+/g adsorbent), q_{max} is maximum adsorption density, K_{ads} is the affinity constant, and {A} denotes the chemical activity of species A. Although many previous studies have used linearization to determine maximum adsorption density and affinity constants, this approach can introduce statistical biases.[36,37] Thus, we used a non-linear regression to determine maximum adsorption density and affinity constants with ISOFIT (Isotherm Fitting Tool).[38]

For synthetic urine, experimental results were evaluated with three competitive adsorption models. The first was the competitive Langmuir model (Equation 5, where n=3 for NH_4^+, Na^+, and K^+).[35] The values of q_{max} and K_{ads} calculated from the single-cation adsorption experiments were used as inputs to the competitive Langmuir model, which was plotted for various activities using non-linear parameterization in MATLAB (8.3.0 R2014A). The second was a three-solute competitive adsorption model based on Jain and Snoeyink (Equation 6, see section S1.1 for more detail); q_{max} and K_{ads} for each cation were from single-cation adsorption experiments, and numerical subscripts denote each cation from lowest (1) to highest (3) maximum adsorption density.[39] The third was the empirical Langmuir-Freundlich model (Equation 7), in which K_{ads} values were from single-solute experiments, and n and q_{max} (one value for all cations) were determined by nonlinear regression on synthetic urine data. For all three models, adsorption

densities were calculated using the experimentally measured equilibrium activities in synthetic urine. To predict equilibrium adsorption densities and activities in undiluted real urine, we used initial activities and model parameters to solve a system of six equations containing model predictions for each cation and mass balances on each cation (section S1.1).

$$q_{f,i} = \frac{K_{ads,i} q_{max,i} \{A_i\}}{1+\sum_{n=1} K_{ads,n} \{A_n\}} \quad (5)$$

$$q_{f,3} = \frac{q_{max,1} K_{ads,3} \{A_3\}}{1+K_{ads,1}\{A_1\}+K_{ads,2}\{A_2\}+K_{ads,3}\{A_3\}} + \frac{(q_{max,2}-q_{max,1}) K_{ads,3} \{A_3\}}{1+K_{ads,2}\{A_2\}+K_{ads,3}\{A_3\}} + \frac{(q_{max,3}-q_{max,2}) K_{ads,3} \{A_3\}}{1+K_{ads,3}\{A_3\}} \quad (6)$$

$$q_{f,i} = \frac{K_{ads,i} q_{max} \{A_i\}^n}{1+\sum_{n=1} K_{ads,n} \{A_i\}^n} \quad (7)$$

Material cost for different adsorbents was evaluated as an initial analysis of feasibility. Three major determinants of adsorbent cost per gram nitrogen recovered (P_N) were considered: specific adsorbent price ($P_{adsorbent}$, in USD/kg resin), adsorption capacity (q_0 in mmol N/g adsorbent), and number of uses before adsorbent replacement (N) (Equation 8, where MW_N is the molecular weight of nitrogen). Adsorption capacities were the highest values measured in undiluted real urine; resin prices were determined from literature (Table S5). Adsorbent cost per gram nitrogen was also converted to cost per liter of urine treated (P_U) by considering the total ammonia concentration in urine in mg N/L ($[NH_3]_{tot}=[NH_4^+] + [NH_3]$, Equation 9).

$$P_N = \frac{P_{adsorbent}}{N q_0 MW_N} \quad (8)$$

$$P_U = P_N [NH_3]_{tot} \quad (9)$$

For each adsorbent tested, experimental adsorption density values were used to determine the reactor volume (Equation 10). D_U is urine production rate per person (L urine/(person*day)), P_H is average household size (people/household), t_c is time between collection, q is experimental adsorption density (mg NH_4^+-N/g adsorbent), and ρ_b is bulk density (g adsorbent/L reactor

volume). We assumed that the ion exchange cartridge would be replaced weekly and treat 28 liters of urine per week for a household with four people each producing one liter of urine each day. Bulk densities were determined by weighing known volumes of packed adsorbents.

$$V_R = \frac{D_U * P_H * t_c * [NH_3]_{tot}}{q * \rho_b} \quad (10)$$

2.7 Statistical Analysis

Best-fit Langmuir parameters (q_{max} and K_{ads}) determined from non-linear regression were compared for each pair of adsorbents with a one-way ANOVA and paired t-tests. A similar analysis was performed to compare solutions (pure salt, synthetic urine, and real urine). The single-solute Langmuir isotherm was applied to all solutions for consistency in the statistical analysis (Table S6). Although both q_{max} and K_{ads} were compared for each isotherm, only q_{max} was reported because it was a more conservative indicator of significant differences and was more relevant to high ammonium concentrations in urine. Ammonium adsorption densities in experimental triplicates with undiluted real urine for each adsorbent were also compared with a one-way ANOVA and paired t-tests.

3. RESULTS AND DISCUSSION

3.1 Comparison of Adsorbents at pH 4

Based on experiments with NH_4Cl at pH 4, the four adsorbents exhibited different adsorption capacities (Figure 1a); however, the best-fit maximum adsorption densities were not statistically different ($p > 0.05$). More variability was observed at high concentrations because of high dilution factors (e.g., 1:1000 for highest concentrations); they were accepted because of the redundancy present with sixteen points per adsorption curve. The Langmuir model was used because we expected a finite number of identical adsorption sites for zeolite and the synthetic

resins and previous studies reported it had the best fit for the adsorbents tested.[15,23,26,40] Best-fit maximum adsorption densities and affinity constants are summarized in Table S4 and Figure S2. A similar analysis was performed for NaCl and KCl to determine Langmuir parameters for later use in the competitive adsorption model (Figure S3).

Overall, the adsorption capacities and affinity constants for pH 4 NH_4Cl from this study were higher than those in literature (Table S1, Table S4).[22,23,26,27,29] For natural adsorbents, different sources (e.g. clinoptilolite from Turkey or USA)[22] and pretreatment (pyrolysis temperature and time)[26] could contribute to variation in best-fit Langmuir parameters between studies. For all adsorbents, variation could be due to operation at much higher concentrations that show more of the adsorption curve and the use of non-linear regression for fitting (q_{max} values determined by linearization of the Langmuir isotherm were lower; data not shown). Note that the estimate for the maximum ammonium adsorption capacity for Dowex Mac 3 was significantly higher than the highest value measured directly, which is one limitation of using best-fit parameters to compare isotherms.

3.2 Effect of pH on Ammonium Adsorption

Adsorption results for the pH 9 NH_4Cl solutions are presented in Figure 1b. Although the adsorption densities were higher for the synthetic resins than the natural adsorbents, there were no statistically significant differences between adsorbents due to the high variability observed. Ammonium adsorption isotherms at pH 4 and pH 9 were also not significantly different for any adsorbent, but several observations can be made about the effects of pH on adsorption sites and ammonia speciation. Cation adsorption sites are most effective when negatively charged, which

314 occurs when solution pH exceeds the surface point of zero charge. This effect was especially
315 apparent for Dowex Mac 3, which has a reported pKa of 5 (Table S1), which is between the two
316 pH values tested for NH_4Cl solutions. In the pH 4 solutions, substantially fewer sites were
317 deprotonated than in the pH 9 solutions. Accordingly, fewer sites were available for ammonium
318 adsorption and lower adsorption densities were observed, especially at low equilibrium activities.
319 Similar trends have been reported for clinoptilolite.[41]
320
321 The solution pH also impacted NH_4^+ adsorption by affecting ammonia speciation. Given the
322 proximity of the pH in pH 9 NH_4Cl, synthetic urine, and real urine experiments to the NH_3/ NH_4^+
323 pK_a (9.25), up to 35% of total ammonia was present as NH_3. Because NH_3 is uncharged and thus
324 does not participate in cation exchange, we expected the adsorption density to be lower for the
325 pH 9 solutions than the pH 4 solutions. Although this was the trend for the natural adsorbents, it
326 was not the case for the synthetic resins. One possible reason for the difference is that natural
327 adsorbents have more heterogeneous adsorption sites and initial adsorbates and therefore more
328 complex pH effects (Figure S4).
329
330 In interpreting the pH results, it is important to note that the final pH of the solutions, after
331 adsorption equilibrium was established, was different in some cases than the initial solution pH;
332 the equilibrium pH values of the highest concentrations tested for each solution are shown in
333 Figure S5. The equilibrium pH was affected by two competing phenomena. The first was
334 sorption of NH_4^+, which removes it from solution and shifts the NH_3/ NH_4^+ equilibrium, causing
335 protonation of some NH_3 and increasing solution pH. The second was desorption of protons due
336 to exchange with other cations, which decreases solution pH. For the pH 4 solutions, the solution

pH decreased after equilibrating with the synthetic resins, indicating that desorption of protons was the dominant effect. With natural adsorbents exposed to pH 4 solutions, the pH increased, indicating that NH_3/ NH_4^+ equilibrium dominated. In addition, natural adsorbents were initially loaded with a mixture of protons and other cations, leading to relatively fewer H^+ desorbing. Batch experiments with sulfuric acid confirmed this phenomenon, as Na^+, K^+, and Ca^{2+} ions desorbed from natural adsorbents but not from synthetic resins (Figure S4). At pH 9, the NH_3/ NH_4^+ pair buffered the pH and only small pH changes were observed (Figure S5). Synthetic urine and real urine pH values also increased (slightly) for natural adsorbents and decreased for synthetic resins (Figure S5).

3.3 Effect of Competition on Ammonium Adsorption

The effect of competition was investigated by performing adsorption experiments in synthetic urine, in which Na^+ and K^+ competed with NH_4^+ for adsorption sites (Figure 2). Again, the synthetic resins adsorbed more ammonium per gram than the natural adsorbents. In particular, the maximum adsorption density (q_{max} from best-fit single-solute Langmuir isotherm) of Dowex Mac 3 was significantly higher than the other three adsorbents ($p<0.01$ with Dowex 50; $p<0.0001$ with clinoptilolite and biochar). There was no significant difference between adsorption capacities for the pure NH_4Cl and synthetic urine solutions ($p>0.05$), indicating that the presence of other constituents, including competing ions, did not decrease the adsorption density of ammonium on any of the adsorbents.

Synthetic urine adsorption data were fitted to three models: competitive Langmuir, trisolute Jain/Snoeyink, and competitive Langmuir-Freundlich (Figure 2) and the average relative error

and sum of squared error (SSE) were determined. For clinoptilolite, Dowex 50, and Dowex Mac 3, the Langmuir-Freundlich model had the lowest SSE and best overall fit to synthetic urine data (Table S7), although it overestimated adsorption for clinoptilolite and Dowex 3 at low equilibrium activities (Figure S6). It is not surprising that the Langmuir-Freundlich model was superior because the parameters q_{max} and n (Equation 7) were determined by fitting to the synthetic urine data (using nonlinear regression), whereas the Jain-Snoeyink and competitive models were based exclusively on the q_{max} and K_{ads} parameters determined from single-solute Langmuir fits. For biochar, competitive Langmuir was the best fit overall (Table S7), but it overestimated adsorption at low equilibrium activities (Figure S6). The Jain-Snoeyink model assumes competitive Langmuir behavior below the maximum adsorption densities of sodium and potassium and single-solute Langmuir for ammonium above those adsorption densities. There was not much difference between the competitive Langmuir and Jain-Snoeyink isotherms, primarily because single-solute q_{max} values for Na^+ and NH_4^+ differed by at most 0.74 mmol N/g adsorbent (Dowex 50, Table S4).

The fact that the competitive Langmuir model predicted lower adsorption densities in synthetic urine than were measured could be due to overestimating the impact of competitor cations or because other constituents in the synthetic urine increased adsorption (such as acetate; see section 3.5). Single solute ammonium adsorption densities, which isolate the former effect, were higher than competitive Langmuir models for clinoptilolite (38%), biochar (64%), Dowex 50 (75%), and Dowex Mac 3 (18%). Larger differences between competitive and single-solute models may indicate less homogeneous sites and thus more selectivity for ammonium. Even if adsorption sites are identical, access to them may vary based on macroscopic pore size

383 distributions. Hydrated ionic radius is one proxy for access to adsorption sites;[42] ammonium and
384 potassium ions have smaller radii than sodium ions,[43] allowing the former species to diffuse
385 through smaller pores and access more exchange sites. However, the q_{max} values for NH_4^+ and
386 Na^+ from single-solute experiments were similar (Table S4), suggesting that differences in
387 hydrated ionic radius did not completely explain differential adsorption of cations.
388
389 **3.4 Adsorption in Real Urine**
390 The isotherm trends observed in synthetic urine adsorption were similar to those in real urine
391 (Figure 3a, Dowex Mac 3 > Dowex 50 > clinoptilolite ~biochar). Maximum ammonium
392 adsorption densities (q_{max} from best-fit single-solute Langmuir isotherm) were significantly
393 different for all adsorbent pairs except clinoptilolite and biochar. The Dowex Mac 3 adsorption
394 isotherm had the highest maximum adsorption density ($p<0.001$ for pair-wise comparison with
395 all other adsorbents). To provide a more direct comparison between the adsorbents for the
396 specific case of real urine, and to overcome the variability observed in the isotherms, triplicate
397 adsorption experiments were conducted with undiluted real urine (Figure 3b). Dowex Mac 3 had
398 a statistically higher NH_4^+ adsorption density than all other adsorbents ($p<0.001$ for clinoptilolite
399 and biochar; $p<0.05$ for Dowex 50). Together, these results support the conclusion that Dowex
400 Mac 3 exhibited a higher adsorption density than clinoptilolite, biochar, and Dowex 50. Given its
401 manufactured nature, Dowex Mac 3 was expected to have a higher maximum adsorption density
402 than the heterogeneous natural adsorbents; it was also expected to have a higher maximum
403 adsorption density than Dowex 50 because of its aliphatic resin structure and macropores, which
404 have more surface area available for adsorption than the polystyrene backbone of Dowex 50
405 (Table S1).

406

407 The three competitive models from synthetic urine isotherms were also applied to adsorption in
408 undiluted real urine (Table S8). The Jain-Snoeyink model was best for predicting adsorption
409 densities in real urine. The main reason is because the adsorption density in real urine was lower
410 than that measured in synthetic urine at similar equilibrium activity levels (even though the
411 differences were not statistically significant; see next section). Thus, the Langmuir-Freundlich
412 overestimated adsorption density in undiluted real urine.

413

414 To provide more insight into the differential adsorption of competitor cations (Figure 3b), the
415 adsorption isotherms for NH_4^+, Na^+, and K^+ in real urine on Dowex Mac 3 are shown in Figure
416 4a. As expected given its sixfold (relative to Na^+) or tenfold (relative to K^+) higher molar
417 concentration in urine, ammonium occupied the majority of available sites. Preferential
418 adsorption of NH_4^+ was also observed, as seen by the higher adsorption density of ammonium
419 compared to the other cations at the same equilibrium activity. Similar trends were observed for
420 the other adsorbents, even though they are not reported to have higher affinities for ammonium.

421

422 To confirm that ion exchange was the primary sorption mechanism in real urine, the
423 characteristic free energy of adsorption in undiluted real urine was determined using the
424 Dubinin-Radushkevich isotherm. The free energy of adsorption for every adsorbent was in the
425 ion exchange range (>8 kJ/mol),[36] indicating that ion exchange was a more significant factor
426 than van der Waals interactions (Figure S7).

427

428 **3.5 Comparison of Solutions**

For all adsorbents, there were no statistically significant differences between ammonium adsorption curves in different solutions (Figure 3b, Dowex Mac 3; all other resins, Figure S8, $p>0.05$). Given the higher ionic strength in urine compared to NH_4Cl, we expected less adsorption in real and synthetic urine than the pure salt solutions due to charge screening.[44] However, NH_4^+ adsorption densities in urine solutions were not significantly different than in pure salt solutions when plotted relative to both equilibrium concentration and equilibrium activity, which accounts for ionic strength differences (Figure S9, $p>0.05$). Charge screening can be complicated by several factors: the presence of macropores, because sites deep within macropores are less affected by solution characteristics; net surface charge and the distribution of charged surface moieties; and electrostatic effects of previously adsorbed molecules.[45]

In addition to ionic strength, the presence of organics may also affect ammonium adsorption. Organics have been documented to lead to higher NH_4^+ uptake by ion exchange materials due to a reduction in surface tension that increases access to macroporous sites.[23] In our experiments, synthetic urine contained only acetic acid whereas real urine is known to contain acetic acid as well as amino acids; organic acids have been shown to decrease the surface tension of water.[46,47] Jorgensen and Weatherley also determined that the enhancement of ammonium adsorption was not as large at higher adsorption densities,[23] which is the same trend observed when comparing synthetic and real urine with pure salt solutions. Thus, organic compounds present in synthetic and real urine but absent in pure salt solutions may enhance adsorption density for macroporous sites. Real and synthetic urine adsorption curves were not significantly different ($p>0.05$), indicating that synthetic urine was a sufficient proxy and that the more heterogeneous mixture of organics in real urine did not significantly affect ammonium adsorption.

452

453 **3.6 Continuous Flow Adsorption**

454 While batch experiments were useful for characterizing adsorption isotherms, nutrient recovery
455 from urine using ion exchange would most likely be implemented in continuous-flow column
456 configuration. To complement the batch data, breakthrough curves in continuous-flow columns
457 were generated to compare adsorbents (Figure 5a). In control columns with no resin, NH_4^+ and
458 Cl^- mass balances were within 5% (Figure S10). Calculated adsorption densities were 1.91 mmol
459 N/g for biochar, 2.00 for clinoptilolite, 2.74 for Dowex 50, and 4.23 for Dowex Mac 3.
460 These results are similar to batch results (e.g., Fig 3b), confirming that Dowex Mac 3 had the
461 highest adsorption capacity. Importantly, the ammonia concentrations measured during column
462 experiments were less variable than those measured during batch experiments. Possible reasons
463 include the use of lower dilution factors (e.g., note that less variability is observed for the lowest
464 concentrations, similar to the batch experiments) and the potential for more ammonia
465 volatilization to occur during the 24-h batch tests.

466

467 **3.7 Regeneration**

468 Column regeneration was performed for one cycle as a proof-of-concept and regeneration
469 efficiencies were calculated for each adsorbent. The synthetic resins both showed almost 100%
470 regeneration (Dowex 50 95%, Dowex Mac 3 99%). Clinoptilolite had a regeneration efficiency
471 of 43%, indicating that not all ammonium was eluted; biochar had a regeneration over 100%,
472 indicating elution of initially loaded ammonium or biochar decomposition. These natural
473 adsorbents may still be promising for direct application as a solid fertilizer.[48,49]

474

475 **3.8 Feasibility Assessment**

476 As an initial assessment of feasibility, adsorbent cost was determined for recovering nitrogen by
477 ion exchange according to Equation 8. Material cost for each adsorbent was determined from
478 literature values and the adsorption densities were those determined from the triplicate batch
479 experiments in undiluted real urine (Table S5). Based on the low recovery of ammonium from
480 clinoptilolite, it would likely only be used once; however, better regeneration may be possible
481 with other regenerants or other conditions. Thus, for comparison with synthetic resins, we show
482 adsorbent costs for a single use up to 100 uses assuming 100% regeneration efficiency (Figure
483 5).
484
485 For a single use, clinoptilolite had the lowest adsorbent cost/g N because of its low material cost,
486 even though its adsorption capacity is lower than the synthetic resins. However, a more
487 expensive adsorbent can result in a lower treatment cost if it is more regenerable. For example, if
488 clinoptilolite is used once, treatment would cost $7.40/kg N; if Dowex Mac 3 is used 100 times,
489 treatment would cost $6.00/kg N.
490
491 Adsorbent costs ($/g N) were compared to the cost of conventional nitrogen removal (Figure 5b,
492 dotted line).[50] We are currently investigating other regenerants (e.g., HCl, HNO_3) over many
493 regeneration cycles to more conclusively evaluate long-term regeneration potential and costs.
494 With 100% regeneration efficiency, material costs are at or below the cost of biological nitrogen
495 removal if Dowex Mac 3 is used as few as ten times; the natural adsorbents used only once still
496 have a lower material cost than conventional nitrogen removal. In addition, we expect nitrogen
497 recovery to have additional benefits compared to removal, including revenue generated from

value-added products like fertilizer. The same data in Figure 5b can also be calculated per liter of urine using Equation 9 (Figure S11).

Reactor volume will also impact process costs and feasibility. To treat the urine produced by a family of four over one week, the reactor volume required for Dowex Mac 3 was the lowest (5.3 L), followed by Dowex 50 (5.8 L), clinoptilolite (8.9 L), and biochar (19 L)(Figure S12). Biochar required a much larger reactor volume because of its markedly lower bulk density (Table S5).

This analysis illustrates that the adsorbent costs and reactor volumes may be feasible and that further analysis of the potential for ion exchange adsorbents is warranted. Multicomponent models like the Jain-Snoeyink can help predict adsorption capacities based on influent urine concentrations, which can vary (Figure S13). Many other factors besides regeneration potential and adsorption density will affect the cost of recovering nitrogen via ion exchange, including other materials for producing cartridges and regeneration facilities, whether the adsorbents are installed at individual toilets or at the building scale, the cost of regenerant, transport distances, and the final fertilizer product quality and market value. Because the other factors are relatively independent of adsorbent material, however, the simple analysis presented here is useful for comparing adsorbents used in the same configuration, which was the overall objective of this investigation.

3.9 Potential Implications for Urine Treatment

Characterization of four different ion exchange adsorbents has provided a proof-of-concept for nitrogen recovery from source-separated urine via ion exchange. Once their adsorption capacity is reached, natural adsorbents like clinoptilolite and biochar could be applied directly as fertilizer, assuming pathogen concerns can be addressed. Alternatively, ammonium concentrate could be produced by eluting ammonium from any adsorbent. The process modeling conducted in this study can also be used to specify adsorption capacities and regeneration lifetimes required for newly developed adsorbents to be cost effective for nitrogen recovery from urine.

Several process engineering questions are recommended for future research, including optimizing elution of the ammonium to produce a concentrated solution that can feed into fertilizer or other products, and how to combine ion exchange with other nutrient recovery processes, like struvite precipitation. These questions are best investigated using column operation. Additional post-treatment, such as pharmaceutical removal from the eluent or eluate, or converting liquid fertilizer to solid, may be desirable and will affect process costs.

Ion exchange adsorbents could be employed in on-site or centralized wastewater treatment. A decentralized scheme might involve a service provider that regularly collects and replaces household cartridges and transports them to a centralized regeneration facility. Alternatively, cation exchange adsorbents could be used and regenerated on-site at a central facility at which source-separated urine is collected (by manual transport, such as high-density slums, or via dedicated pipes in a large building). Other implementation factors to consider include variability in urine composition, location of treatment facilities, method and cost of transport, and degree of

542 centralization. For example, lifecycle impacts and costs have recently been modeled for
543 phosphate recovery and trace organic removal via ion exchange.[51]
544
545 Because source separation has not yet been widely adopted, resource recovery technologies like
546 ion exchange can potentially influence the design and scale of source separation systems. In this
547 study we have demonstrated that ammonium can be recovered from urine using ion exchange
548 and compared the efficacy of natural and synthetic adsorbents. Further work on continuous-flow
549 recovery, optimal scale, and integration with other processes will add to the base of knowledge
550 for potential application of novel technologies for nitrogen recovery from source-separated urine.
551 Another promising direction for future research is the recovery of ammonium from other high-
552 strength wastes, such as digestate and agricultural waste streams.
553
554 **ASSOCIATED CONTENT**
555 The Supporting Information (SI) contains single solute adsorption curves, details on isotherm
556 modeling, and calculations and results for financial feasibility. This information is available free
557 of charge via the Internet at http://pubs.acs.org.
558
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562 **Notes**
563 The authors declare no competing financial interests.
564

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703

704

FIGURES

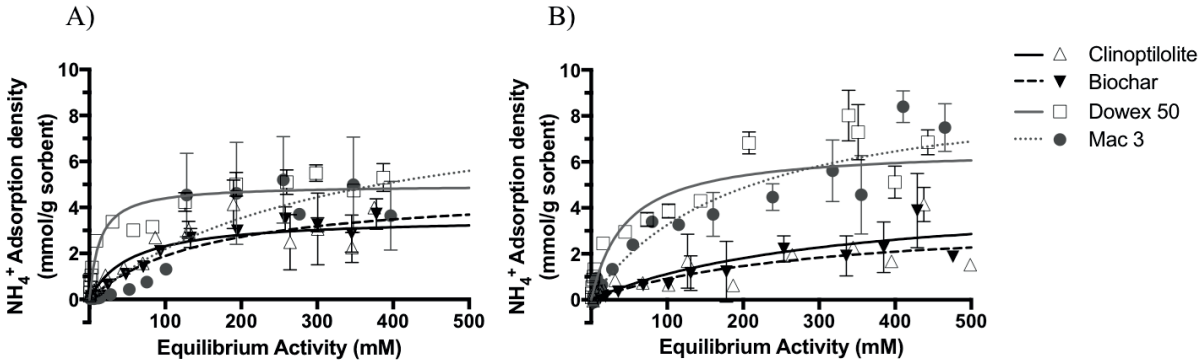


Figure 1. NH_4^+ adsorption in NH_4Cl (a) without pH adjustment and (b) for pH 9 solutions. Error bars represent one standard deviation above and below mean of dilution triplicates (n=3) for high activities (> 100 mM). Curves show best-fit Langmuir isotherms based on non-linear regression of experimental data.

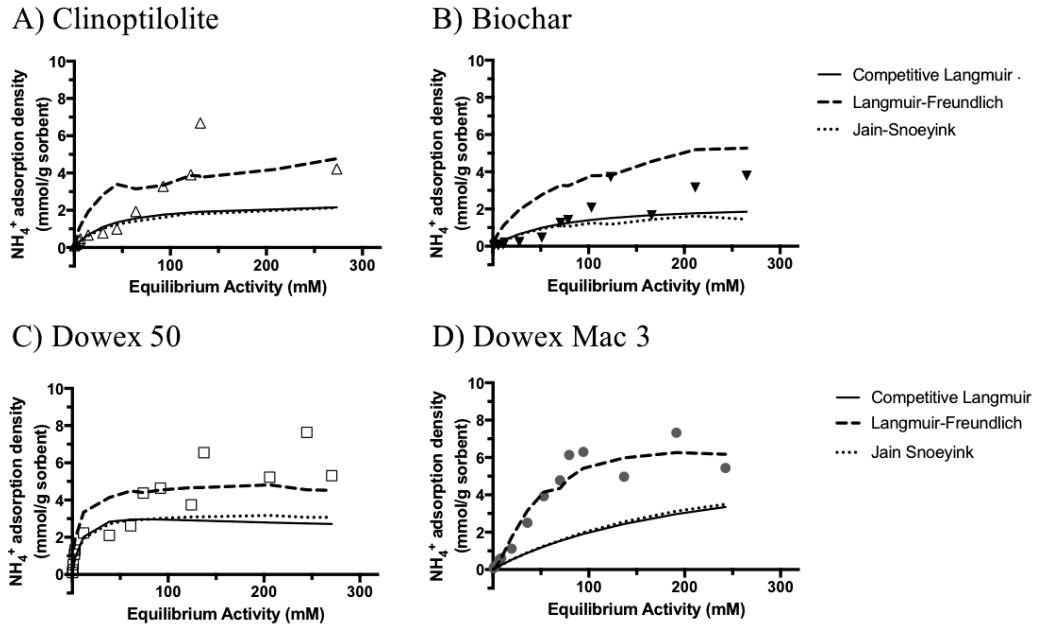
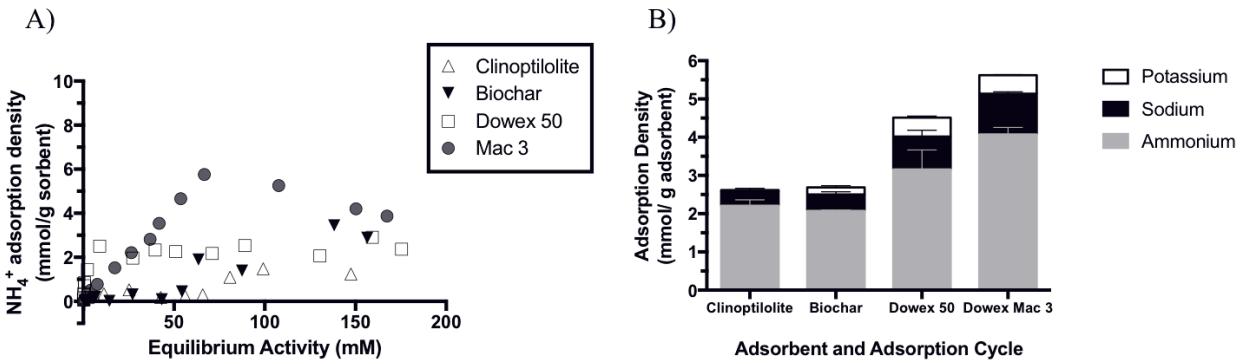


Figure 2. Comparison of NH_4^+ adsorption in synthetic urine and competitive Langmuir, competitive Langmuir-Freundlich, and Jain-Snoeyink models for (a) clinoptilolite, (b) biochar, (c) Dowex 50, and (d) Dowex Mac 3. Insets of lower equilibrium activities are in Figure S6.



716

717 **Figure 3. (a)** NH_4^+ adsorption isotherm for real urine. (b) Adsorption density of NH_4^+, Na^+, and

718 K^+ in undiluted real urine. Error bars represent one standard deviation above and below mean for

719 experimental triplicates (n=3), and in some cases are too small to be shown.

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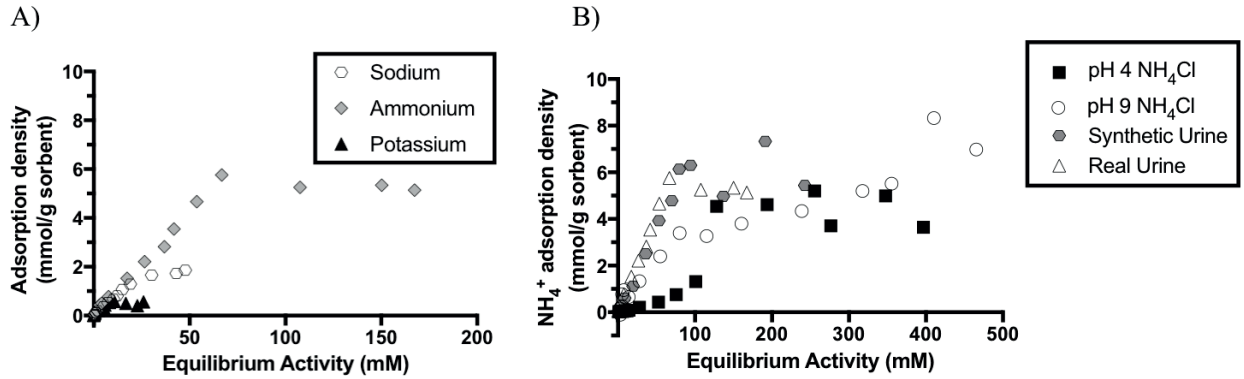

721

722 **Figure 4.** (a) Dowex Mac 3 NH_4^+, Na^+, and K^+ adsorption in real urine. (b) Dowex Mac 3 NH_4^+

723 adsorption for all solutions.

724

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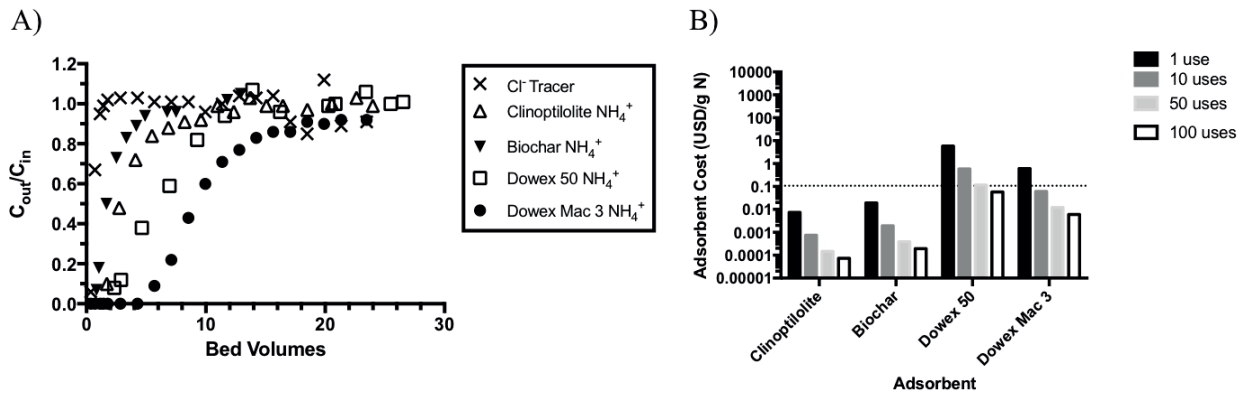

Figure 5. (a) Adsorption breakthrough curves in continuous-flow columns. (b) Comparison of adsorbent cost for all four resins (in USD/g N) assuming 100% regeneration (r=1). The dotted line is the cost of conventional biological nitrogen removal per gram nitrogen removed (horizontal line).[50]