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Evaluating ion exchange for nitrogen recovery from source-separated urine in Nairobi, Kenya

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ABSTRACT

Rapid population growth in developing world urban centers outpaces provision of essential services such as excreta collection and treatment. Separate collection of urine and feces and decentralized treatment can potentially serve more households at lower energy and cost than conventional waterborne sewers and treatment plants. We conducted a technical validation and preliminary economic modeling to evaluate ion exchange columns, one technical option for recovering nitrogen from urine in Nairobi, Kenya. This technology could be combined with phosphorus recovery and a disinfection step to allow local discharge of the treated urine. Performance, as measured by adsorption density (4.02–4.21 mmol N/g resin) and regeneration efficiency (> 90%) of the adsorbent, was consistent over ten adsorption-regeneration cycles and with columns ten times larger than lab-scale (65 L/d vs. 6.5 L/d). Effluent absorbance and electrical conductivity were identified as indicators of urine and ammonia breakthrough, respectively; both parameters are lower cost and easier to measure on-line than ammonium concentrations. Urine storage containers should be closed to avoid changes in urine composition, including loss of ammonia (and thus potential revenue). Treatment of urine by ion exchange is 40% less expensive than disposal without treatment and urine-derived ammonium sulfate was produced well below market costs of commercial fertilizers.

1. Introduction

The majority of people in the developing world live with untreated feces and urine in their communities (Baum et al., 2013). Urban centers in developing countries are expected to experience a disproportionately large share of population growth that is likely to continue to outpace provision of services such as water supply and sanitation (Jacobsen et al., 2012). The proportion of urban residents who live in informal settlements has remained constant at 72% in sub-Saharan Africa (Jacobsen et al., 2012); residents of these high-density, unplanned settlements are particularly vulnerable to water and excreta-related diseases. Excreta collection and treatment can improve human health and environmental quality by reducing the transmission of these diseases and avoiding nutrient discharges that irreversibly alter aquatic environments (Nelson and Murray, 2008). Globally, estimated costs to society from inadequate sanitation are \$260 billion per year due to associated health care, premature deaths, and productivity losses

(Hutton, 2012).

With only 10% of sub-Saharan Africans connected to sewer systems and less than 50% expected by 2050 (Larsen et al., 2016; Morella et al., 2008), universal coverage with conventional sewers and centralized wastewater treatment is an unrealistic proximate goal. Decentralized collection and treatment may be less costly and require less energy while providing opportunities for revenue generation through resource recovery from waste (Nansubuga et al., 2016). An approach in which sanitation providers aim to improve public health, environmental quality, and profit may accelerate and sustain sanitation access. Valuable nutrients (e.g., nitrogen, phosphorus, potassium) can be extracted from human excreta. They are especially valuable near Nairobi, Kenya, where agricultural soil nutrient levels are low due to over-farming, population density, and poor water quality (Stoorvogel et al., 1993). These constraints create high demand for manufactured fertilizers, which the Kenyan government has subsidized since 2009 (Kenya Fertilizer Assessment, 2012; Shimeles et al., 2015). Despite these

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subsidies, fertilizers are often underutilized by the average Kenyan farmer because of high import and transport costs (Van den Bosch et al., 1998), limited fertilizer supply (Ochola and Fengying, 2015), distance to fertilizer distribution channels (Jayne et al., 2003), and cumulative soil degradation (Marenya and Barrett, 2009).

Separate collection of urine facilitates nutrient recovery and fertilizer production because urine contains the majority of excreted macronutrients but is typically only 1% of wastewater volume (Friedler et al., 2013). Phosphorus is an increasingly scarce fertilizer component that can be recovered from urine through precipitation of struvite (magnesium ammonium phosphate, MgNH_4PO_4) (Etter et al., 2011). Nitrogen can be recovered from urine using several techniques, including urea stabilization (Randall et al., 2016), electrochemical stripping (Tarpeh et al., 2018a), nitrification-distillation (Udert and Wächter, 2012), and ion exchange (Tarpeh et al., 2017). During urine storage, nitrogen in the form of urea is hydrolyzed to ammonium (NH_4^+) (Udert et al., 2003), which is retained on the ion exchange adsorbent's negatively charged sites. Once loaded with NH_4^+ , cation exchange adsorbents could be applied as solid fertilizers (if naturally derived) or regenerated to produce liquid fertilizer and reusable adsorbent. In this study, ammonium sulfate fertilizer was produced; other options include ammonium nitrate and ammonium chloride, which can be generated by varying the compound used to elute the adsorption columns. Ion exchange can be applied at various scales, from individual toilets or households to centralized urine collection depots. A previous comparison of adsorbents showed that Dowex Mac 3, a cation exchange resin, has high adsorption density and regeneration efficiency that make it well-suited for ammonium recovery from urine (Tarpeh et al., 2017).

The goal of this investigation was to determine if producing ammonium sulfate from urine via ion exchange is a viable business model for container-based, source-separated excreta collection and treatment services. Our objectives were to: (i) demonstrate proof-of-concept and measurement methods in the field, (ii) evaluate the implications of urine composition, process indicators, and scalability for urine collection and treatment, and (iii) compare the cost of nitrogen recovery via ion exchange to current excreta management and fertilizer production practices in the study region.

2. Materials and methods

2.1. Description of field site

The field site for the research was Nairobi, Kenya, where the social enterprise Sanergy operates more than 1000 dry, source-separating, toilets in several informal settlements, as of August 2017. The toilets, branded as Fresh Life Toilets (FLTs), are primarily owned and operated by local entrepreneurs via a franchise business model. These toilets are used over 50,000 times a day and revenues from user payments go to franchisees (Auerbach, 2016). While most toilets are open to the public, some are located at schools and multi-family dwellings. Sanergy charges toilet operators for daily collection of the waste and generates revenue from the sale of excreta-derived products (O'Keefe et al., 2015). The user interface is a squat plate with separate holes for urine and feces; urine and feces containers (25 L urine, 30 L feces) are collected and replaced daily by Sanergy employees. The containers are taken to a central transfer station where urine and feces are processed separately. The fecal waste is transported 30 km by truck to a processing facility where it is converted into several value-added products: a soil additive branded as *Evergrow* through a co-composting process, biogas through an anaerobic digestion process, and a black soldier fly animal feed. Urine from the toilets is stored in 1000-L tanks at the transfer station, which are emptied every 2–3 days and the urine is trucked 20 km to a wastewater treatment facility.

2.2. Synthetic and real urine composition

Synthetic stored urine was used to validate column operation because its composition was known (Table S1) and constant between locations (Table S2 for preparation method) (Tarpeh et al., 2017; Udert et al., 2003). Real urine from different locations (Nairobi, Kenya; Dubendorf, Switzerland; Berkeley, California, USA) and collection systems was compared to determine the effects of varying urine composition and collection methods on urine treatment. In Berkeley, urine from participants was collected individually from approximately 20 volunteers (male and female), homogenized in sterile containers, and stored in closed containers (Committee for Protection of Human Subjects, Protocol 2016-10-9284). In Nairobi, source-separated urine from eight urine-diverting dry toilets and centralized collection tanks was analyzed. In Dubendorf, multiple waterless urinals and urine-diverting flush toilets in a building drained to a single collection tank, from which samples were drawn.

Urea hydrolysis to total ammonia ($\text{NH}_3/\text{NH}_4^+$) proceeded spontaneously in collection systems (Dubendorf (Udert et al., 2003) and Nairobi (this study)); 10 mg/L jack bean urease (Sigma Aldrich, St Louis, MO) was added to Berkeley urine to accelerate the process (Mobley et al., 1995). Berkeley urine was analyzed and used in ion exchange after 5 days of storage, and analyzed again after one month of storage. Magnesium and calcium concentrations were measured as negligible in stored urine via ion chromatography, presumably due to spontaneous struvite and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) precipitation (Udert et al., 2003).

2.3. Column experiments

Columns were constructed and operated according to our previous studies that achieved high ammonium adsorption density and recovery efficiency (Tarpeh et al., 2018b, 2017). Briefly, upflow continuous adsorption experiments were performed in plastic columns (2.54-cm diameter, 16-cm length, PVC plastic) packed with Dowex Mac 3 (63.5 ± 1.5 g), a cation exchange resin. After pretreatment with 10 mL of 1 M borate buffer per gram of resin, either synthetic or real urine (from closed tanks at transfer station) was pumped at 4.5 mL/min (6.5 L/d, 0.0148 cm/s) through each column for 6 h, and 2-mL effluent samples were collected every 20 min and analyzed for ammonium. Adsorption densities were calculated by numerically integrating breakthrough curves to determine the total mass of ammonium retained by the columns, and dividing by resin mass (Equations S1–S2). The hydraulic performance of columns was verified in experiments with synthetic urine and measurement of chloride as a conservative tracer.

Regeneration experiments were performed using 0.1 M (0.65%) H_2SO_4 , pumped at 22.5 mL/min for 2 h, to elute the ammonium from the columns after they were saturated (Tarpeh et al., 2018b, 2017). The total volume of eluent was larger than the volume of urine treated; while this approach is impractical for implementation, it was useful for our goal of identifying the maximum amount of nitrogen that could be recovered. Strategies for generating more concentrated final product, including reusing product as eluent and applying reverse osmosis, are currently being explored. Effluent was combined over the course of the experiment and ammonium concentration was measured in the composite sample. Regeneration efficiencies were calculated by dividing the mass of ammonium eluted (product of composite concentration and effluent volume) by the mass of ammonium adsorbed in the previous cycle (Equation S3).

Ten adsorption-regeneration cycles were conducted in triplicate to evaluate regeneration lifetimes with real urine collected from FLTs. For each cycle, adsorption densities and regeneration efficiencies were calculated using the methods above.

Performance at larger scale (scaling factor of 10) was investigated with larger columns (5.08-cm diameter, 40-cm length, 601 ± 25.2 g resin) and flow rates (65 L/d), with the same laboratory set-up and

Table 1

Digestate and urine composition (closed tank). All concentrations in mg/L except for pH and EC (mS/cm). SEM values in parentheses.

	Digestate	Urine
pH	8.45	9.00 (0.02)
EC	23.5	35.9
COD	5790 (1070)	8640 (61.1)
Na ⁺	628 (3.11)	2520 (104)
NH ₄ ⁺ -N	3030 (9.60)	6420 (138)
K ⁺	1530 (9.74)	2750 (76.9)
Cl ⁻	786 (18.7)	4840 (154)
PO ₄ ³⁻ -P	616 (14.1)	1040 (21.8)

analysis methods as for the 2.54-cm diameter columns. Larger columns were constructed in Nairobi from locally available PVC plastic. The objective of these experiments was to validate the ammonium recovery process at larger scales that may be more relevant to centralized nitrogen recovery in the Sanergy container-based system.

Column experiments were also conducted with anaerobic digester effluent for comparison to real urine. Digestate is produced during anaerobic digestion of feces and has high ammonia concentrations (Table 1), making it another potential liquid stream for nitrogen recovery via ion exchange.

2.4. Chemical analysis

In Berkeley, total ammonia nitrogen (TAN; NH₃ + NH₄⁺), sodium, and potassium, magnesium, and calcium were measured via cation chromatography (Dionex, IonPac CS12 column, 30 mM methanesulfonic acid eluent, 1.0 mL/min, 40 °C) for column experiments conducted in Berkeley and influent urine samples from Nairobi (Tarpeh et al., 2017). In Nairobi, Hach kits were used to measure total ammonia nitrogen (salicylate method 10031).

Chloride, phosphate, and sulfate were measured in Berkeley by anion chromatography (Dionex, IonPac AS23 column, 4.5 mM NaHCO₃/0.8 mM Na₂CO₃, 1.0 mL/min, 30 °C) (Tarpeh et al., 2017). In Nairobi, Hach kits were also used to measure potassium (method 8049), chemical oxygen demand (COD, method 8000), and phosphate (method 8190). Samples from column experiments performed in Nairobi were measured in Nairobi after at most 24 h storage at 4 °C. pH and electrical conductivity (EC) were measured with a pH/EC/ORP meter (H12211 m, Hanna Instruments, Padova, Italy). For all chemical analyses, methods were validated at less than 5% error on standard solutions.

To minimize ammonia volatilization in influent urine samples that were collected in Nairobi and measured in Berkeley, samples were preserved in closed containers (both parafilm and lids) with minimal headspace at 4 °C for approximately two weeks. Total ammonia was used as a quality control parameter to measure differences between

influent urine samples measured in Nairobi with Hach kits, in Berkeley with Hach kits after transport, and in Berkeley with ion chromatography after transport. Because total ammonia concentrations varied less than 10% between the three measurement methods, they were considered equivalent. Because ammonia was the parameter most likely to vary (Udert et al., 2006), other parameters were assumed to remain constant during sample storage. While phosphate sorption to plastic storage containers may have occurred, precipitates were not observed during sample storage.

2.5. Statistical analysis

For all comparisons of breakthrough curves, one-way ANOVA and paired t-tests were used to compare the slope of breakthrough curves and time to breakthrough. Two-tailed analyses were used with a significance level of $p = 0.05$. For urine composition, the standard error of the mean (SEM) was calculated for triplicate measurements.

3. Results and discussion

3.1. Comparing lab and field nitrogen recovery

Synthetic urine was used to compare ammonium breakthrough curves measured with cation chromatography (Berkeley) and Hach methods (Nairobi). There were no significant differences between calculated adsorption densities nor slopes of breakthrough curves (Fig. 1a), indicating that column setups and column operation were similar in Berkeley and Nairobi.

For real urine, breakthrough was observed in fewer bed volumes with Nairobi urine than Berkeley urine (Fig. 1b). Because the adsorption densities and slopes of breakthrough curves were not statistically different for synthetic urine, the differences between real urine breakthrough curves in Berkeley and Nairobi were attributed to variation in urine composition. The fewer bed volumes to breakthrough observed in Nairobi urine can be explained by higher ammonia concentrations (see section 3.4.1), which leads to adsorption sites filling faster (Onyang et al., 2009). The higher ammonia concentration in Nairobi urine was likely due to a less hydrated population and the collection method. Based on drinking water in Kenya being less accessible than in the U.S., drinking water intake in Kenya is likely much lower, leading to more concentrated urine (Rose et al., 2015). Berkeley urine was collected in one day and stored; in Nairobi, each day's urine was added to a larger volume of already hydrolyzed urine. Urease-containing bacteria were likely present at higher concentrations in Nairobi containers due to multiple uses; in addition, urease is not consumed during urea hydrolysis (Mobley et al., 1995), meaning that hydrolyzed urine contains urease that could rapidly hydrolyze the fresh urine added each day in Nairobi.

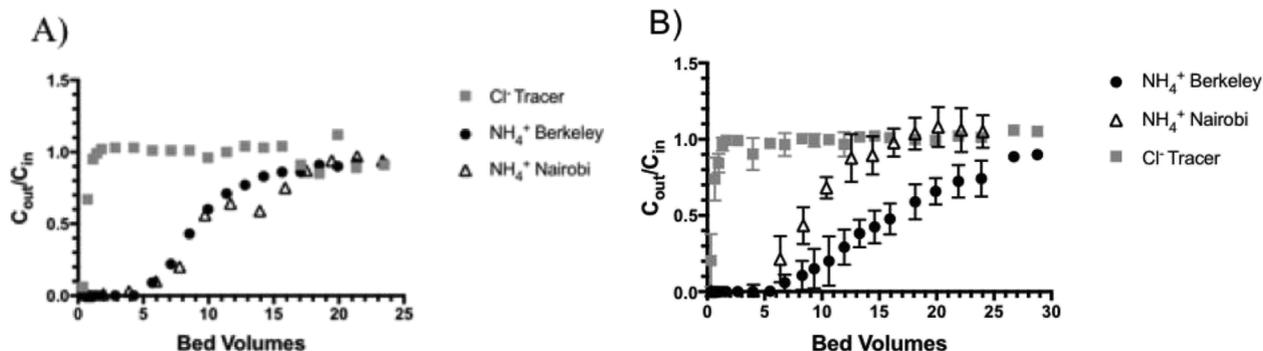


Fig. 1. Adsorption breakthrough curves for (a) synthetic urine and (b) real urine in Berkeley and Nairobi. Chloride curves are from Berkeley experiments. Figure a is for one experimental replicate; Figure b reports results from triplicate columns (± 1 standard deviation; some error bars too small to see).

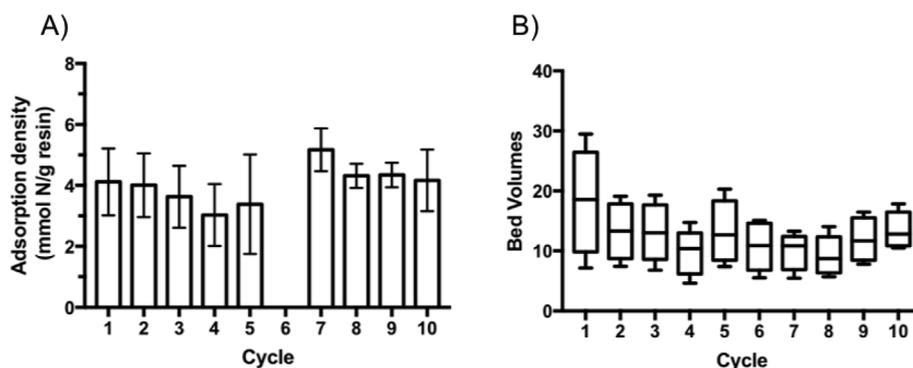


Fig. 2. (a) Average adsorption density vs. cycle for triplicate columns. Error bars indicate ± 1 standard deviation. (b) Average number of bed volumes for 10%, 25%, 50%, 75%, and 90% breakthrough for each cycle.

3.2. Repeated adsorption and regeneration

There was no significant decrease in adsorption density over ten adsorption-elution cycles (Fig. 2), indicating Dowex Mac 3 resin could be regenerated at least ten times. The average adsorption density for all cycles and columns was 4.02 ± 0.19 mmol N/g resin, which was within 3% of repeat adsorption density measured in Berkeley of 4.14 mmol N/g resin (calculated from Berkeley NH_4^+ curve in Fig. 1b). During cycle 6, flow through all columns slowed to below 1 mL/min, likely due to a pressure increase from resin swelling (DOWEX MAC-3 Engineering Information, 2003) or biofilm growth. To restore flow, approximately 12 g resin (approximately 20% of total resin) was removed from each column; resin mass was adjusted in adsorption density calculations for subsequent cycles. Given its exceptionally low flow rate, cycle 6 was not included in average adsorption density calculations. Based on the observed slowing of flow rate in all three experimental replicates, evaluating resin swelling and biofilm growth are high priorities for future work at pilot scale.

With the exception of cycles 5 and 6, all experiments reached greater than 90% breakthrough ($C_{\text{out}}/C_{\text{in}} > 0.9$). The majority of regeneration efficiencies were above 90%, indicating successful elution of ammonium from the resin to create ammonium sulfate (Fig. S1). Lower regeneration efficiencies (e.g., cycles 1, 6, 7) were not significantly different than the mean for all other cycles and more likely resulted from measurement error or error propagation during calculations than from residual ammonium. If ammonium remained after a given regeneration experiment, we would expect a decrease in adsorption density during the next cycle; however, this phenomenon was not observed (Fig. 2).

3.3. Scalability

Nitrogen recovery via ion exchange could be implemented at individual toilets, a centralized collection center, or at semi-centralized transfer centers. This modularity makes ion exchange an attractive option for container-based sanitation services. At the time of the field

study (July 2016), the average Sanergy toilet collected 6.4 L of urine per day (Equation S4), very close to the lab-scale flowrate (6.5 L/d) in this investigation. The adsorption-elution process was also performed at a scale ten times larger (flow rate and resin mass) to mimic conditions relevant for a transfer or collection center. The adsorption density (4.21 mmol N/g resin, range 3.89–4.52 mmol N/g resin) and regeneration efficiency (103%, range 96.8–110%) for columns scaled up by a factor of ten were within 5% of those observed at small scale (4.02 ± 0.19 mmol N/g resin; $102 \pm 9.5\%$ regeneration efficiency), indicating similar performance at both scales.

Adsorption densities at both scales were within 5% of predicted adsorption density (4.20 mmol N/g resin) (Tarpeh et al., 2017), which was interpreted as efficient use of resin in the columns. Predicted adsorption density was based on an adapted three-solute Jain-Snoeyink isotherm, which accounts for the influence of sodium and potassium on ammonium adsorption during cation exchange with urine (Section S1.3). As of August 2017, Sanergy collects 6000 L of urine per day, which could be treated by 60 parallel columns that each treat 100 L/d. A smaller number of larger-volume columns could also be used. Results from experiments at different scales inform implementation tradeoffs such as column dimensions, number of columns, and degree of centralization that can be evaluated in future research.

3.4. Implementation considerations

3.4.1. Urine composition

Urine can vary in salt concentrations, pH, and color. To determine the effects of urine variation on implementation of nitrogen recovery, we compared urine composition in several Sanergy toilets, throughout the Sanergy collection system (collection containers and depot storage tanks), and in three unique collection schemes (Nairobi, Dubendorf, Berkeley).

Table 2 provides an overview of the ionic composition of urine from eight individual FLT's. The containers were sampled on the day of collection (< 24 h storage). The average pH was 9.00 ± 0.02 . The average total ammonia concentration was 6560 mg/L NH_4^+ -N (range

Table 2

Characteristics of urine in individual toilets, *Ammonium sample number, n = 7 not 8. All measured on IC in Berkeley.

Urine source	Chloride mg Cl/L	Phosphorus mg PO_4^{3-} -P/L	Sulfate mg SO_4 /L	Sodium mg Na/L	Ammonium* mg NH_4^+ -N/L	Potassium mg K/L
Toilet 1	4660	1270	1420	3320	7040	2750
Toilet 2	3950	1100	1300	2660	5480	2130
Toilet 3	4360	1480	1740	3760	n.a.	3430
Toilet 4	3320	1210	1430	2670	6560	1840
Toilet 5	5460	971	1380	3890	6260	2480
Toilet 6	6670	1130	1440	4140	6110	2710
Toilet 7	4880	1110	1600	3070	7890	2610
Toilet 8	5470	1050	1370	3980	6600	2850
Mean (SEM, n = 8)	4840 (366)	1170 (55.2)	1460 (50.4)	3440 (209)	6560(287)	2600 (169)

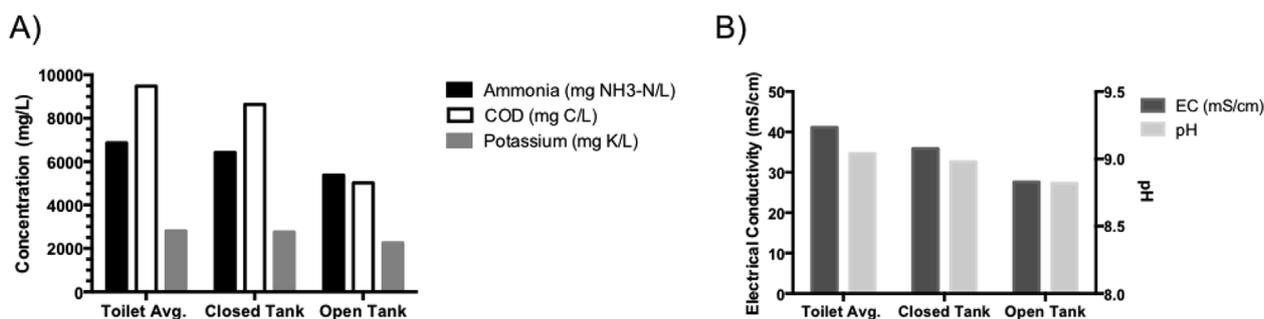


Fig. 3. Comparison of urine composition from average of individual toilets, closed storage tank, and open storage tank.

of 5480–7888 mg/L $\text{NH}_4^+\text{-N}$, SEM = 287) and average phosphate was 1170 mg/L $\text{PO}_4^{3-}\text{-P}$ (range of 971–1480 mg/L $\text{PO}_4^{3-}\text{-P}$, SEM = 55.2). The high ammonium concentrations indicated that most of the urea present in the freshly excreted urine was hydrolyzed by bacteria to $\text{NH}_3/\text{NH}_4^+$ in the approximately 24 h between urine collections. Rapid hydrolysis of urea to ammonia is likely due to the presence of urease from bacteria in urine (commonly 5×10^8 cells/mL) (Lahr et al., 2016) and from fecal cross-contamination (Schönning et al., 2002). Average chloride, sodium and potassium concentrations had a larger variation than phosphate, sulfate and ammonium. Measured ion concentrations were similar to those reported in previous studies (Udert et al., 2006).

Urine composition was also compared between individual toilets (average of the eight toilets reported above) and the large collection tanks at the current centralized urine depot. Ammonia, COD, electrical conductivity, and pH were higher at individual toilets than collection tanks; the same parameters were higher for closed tanks than those left open (Fig. 3). These trends primarily result from volatilization of NH_3 , carbon dioxide (CO_2), and volatile organic compounds, which are common problems that alter urine composition and cause odor in urine collection systems (see section S1.4) (Zhang et al., 2013). pH is expected to decrease due to NH_3 , a base, leaving the aqueous phase (Equation S11). Electrical conductivity decreases were likely due to spontaneous precipitation of inorganic salts (e.g., struvite, hydroxyapatite) and accumulation of biomass in hydrolyzed urine (Equations S12 and 13). These solids have been regularly detected during urine collection (Etter et al., 2011; Tarpeh et al., 2018b; Udert et al., 2003); in this study, solids were observed in collection tanks but not analyzed for composition. CO_2 volatilization, which reduces electrical conductivity by 2 mol for every mole CO_2 volatilized, could also contribute to observed decreases in electrical conductivity (Equation S14). COD likely decreased due to volatilization of CO_2 and organic compounds such as trimethylamine (Troccaz et al., 2013), as well as microbial assimilation and metabolism. The difference in TAN, COD, pH, and EC between toilets and closed tanks was smaller than the difference between closed and open tanks. Urine storage is usually required for urea hydrolysis; however, high total ammonia concentrations in individual toilet samples indicate that the majority of urea is hydrolyzed in the 24-h period between container collections. Residual biofilms may form in containers or on squat plates, including bacteria that contain urease and hydrolyze urea quickly. Urine containers for each toilet are washed with soap and water before reuse; however, 1000-L urine storage tanks are not washed and thus foster growth of biofilms and bacteria in sediments.

These compositional differences in urine within the Sanergy collection system are important to consider for the ion exchange process because loss of ammonia translates to a loss of revenue, which could impact the business model for a fertilizer product. While ammonia is lost in collection and storage, the effect of open storage containers (1000 L) is larger than the effect of open collection containers (25 L). To reduce ammonia losses, storage containers should remain closed as much as possible at the centralized treatment station.

We compared total ammonia concentrations in urine collected for

laboratory experiments in Berkeley, California, USA; urine from waterless urinals and low-flush urine-diverting toilets in Dubendorf, Switzerland; and urine collected in a waterless, container-based system in Nairobi, Kenya (Fig. S2). For the samples from Nairobi, closed storage tank values are shown. Nairobi samples were more concentrated than urine from Berkeley and Dubendorf. Dilution by flush water is one reason for the lower concentrations observed in Dubendorf; incomplete urea hydrolysis may explain those in Berkeley. Samples taken later from stored Berkeley urine showed higher concentrations (7000 mg N/L vs. 4000 mg N/L), further supporting incomplete urea hydrolysis as the source of lower ammonium concentrations. Urine composition data are useful for predicting adsorption density and breakthrough times for planning ion exchange columns in different regions and urine collection systems.

3.4.2. Process indicators

Measuring ammonia can be time-consuming and requires laboratory equipment and expertise. Process indicators that might be easier or less expensive to measure, including electrical conductivity, pH, and absorbance (color), were also explored. These benefits may be especially significant in decentralized recovery schemes and resource-constrained communities. In particular, the current approach to creating breakthrough curves requires measuring total ammonia nitrogen for several regularly spaced samples; on-line monitoring of a process indicator could provide a more robust, automated solution.

Color and electrical conductivity differ between stored urine and pretreatment solution (1 M borate buffer), making them potentially useful indicator parameters. Effluent absorbance was a useful indicator for urine because stored urine was brown while the borate buffer used to pre-treat the columns was clear. In three different adsorption experiments, absorbance increased around one bed volume (Fig. 4a). Thus, measuring absorbance is an alternative to measuring chloride as a conservative tracer in cation exchange columns. Effluent electrical conductivity was a better indicator for ammonium breakthrough (Fig. 4b). Electrical conductivity showed two increases: the first around one bed volume, and the second mirrored ammonium breakthrough. The first increase was due to constituents in urine, which was more conductive than pretreatment solution. Because ammonium was retained on the resin, this effluent had a slightly lower electrical conductivity than influent synthetic urine; the second increase accounts for the difference once the resin was exhausted. Electrical conductivity has also been demonstrated as an effective indicator of urea hydrolysis due to the appearance of ammonium and consumption of urea (Ray et al., 2017). pH was not indicative of ammonium breakthrough because the pretreatment solution had a similar pH to synthetic urine (both 8.5–9, Fig. S3). Based on these results, we concluded that effluent absorbance at 585 nm was a conservative tracer for urine and electrical conductivity could be measured to monitor ammonium breakthrough.

3.5. Business model evaluation

Three potential value propositions exist for recovering nitrogen

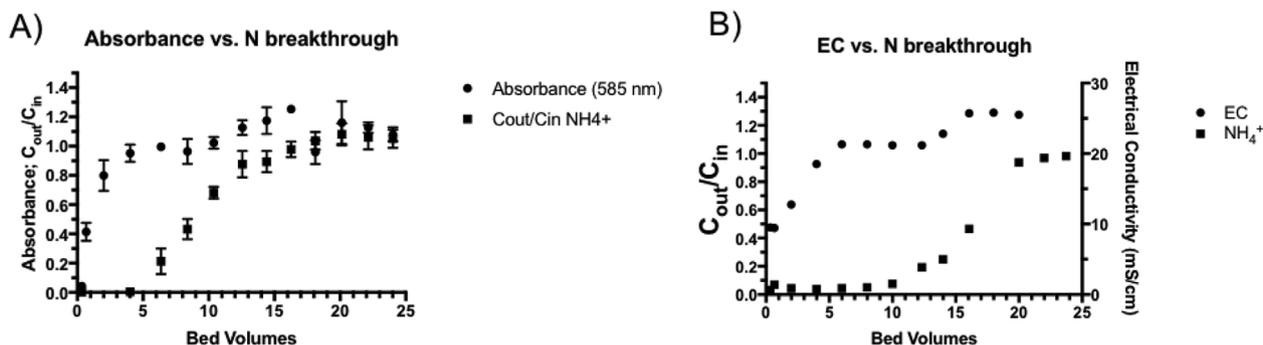


Fig. 4. (a) Absorbance at 585 nm and (b) electrical conductivity vs. ammonium breakthrough curves. Error bars indicate one standard deviation above and below for figure A; some error bars are too small to be shown. For Figure 4b, only one replicate measured and shown.

from urine with Sanergy: (1) reducing urine exhaustion volume and cost, (2) supplementing solid organic fertilizer with nitrogen, and (3) creating a separate nitrogen fertilizer product.

Resin and regenerant are the primary contributors to cost for the ion exchange process because they require continuous, long-distance supply chains. As a growing urban center in East Africa, Nairobi is one of the most likely regions to overcome the obstacles of establishing industrial supply chains. Based on its size, substantial international connections, and experience marketing its soil additive Evergrow, Sanergy is well-positioned to create supply chains through bulk purchases of resin or increasing demand with accelerating adoption of ion exchange processes. Other elements, including plastic housing and pumping, are available locally and are inexpensive by comparison. Transporting urine from toilets to a treatment facility also affects cost; however, daily collection of urine and feces containers already occurs in the Sanergy business model. While resin costs are constant whether ion exchange occurs at individual toilets or the transfer station, collecting nitrogen in a concentrated form (on resin) reduces transport costs compared to collecting untreated urine from each toilet because of the high water content (96% (Drangert, 1998)) of urine.

In principle, removing nitrogen and phosphorus from urine, with discharge to water bodies or leaching to soil, could replace trucking urine to wastewater treatment plants (i.e., urine exhaustion). Treatment of urine by ion exchange would improve upon the common practice of discharging untreated urine to the environment by attenuating nutrient emissions (Udert et al., 2015); our results demonstrate that the technology could meet existing regulations in Kenya for discharge to the environment (100 mg/L Total Kjeldahl Nitrogen (Environmental Management And Co-Ordination (Water Quality) Regulations, 2006)). However, ion exchange has not yet been evaluated to determine if pathogen removal occurs. Urine exhaustion currently costs 1100 KES/m³ (~10.7 USD/m³). Dowex Mac 3 resin costs decrease with number of uses from 22 (10 uses) to 2.20 USD/m³ urine (100 uses, Equation S15). Constant performance was observed for ten adsorption-regeneration cycles (see section 3.2) and calculated for 100 cycles for comparison; the resin has not yet been validated for 100 cycles. Sulfuric acid for regeneration costs an additional 4.20 USD/m³ urine (Equation S16); thus, Dowex Mac 3 resin and regeneration costs total 6.40 USD/m³ urine (Equation S17). To ease comparison with fertilizer prices, urine exhaustion and ion exchange costs were converted to USD/kg N (Equation S18) and are shown in Fig. 5. Global average wholesale prices were used for resin and regenerant costs because the resin and ammonium sulfate are not commonly available in Kenya. Ion exchange treatment was 40% less expensive than exhaustion to a wastewater treatment facility that only partially removes nitrogen, emitting the rest to aquatic environments. Thus, ion exchange is a cost-effective option for treating urine to produce value-added fertilizers and avoid nutrient discharges compared to the current method of trucking urine to a wastewater treatment facility.

Ion exchange costs could be further optimized to reduce processing

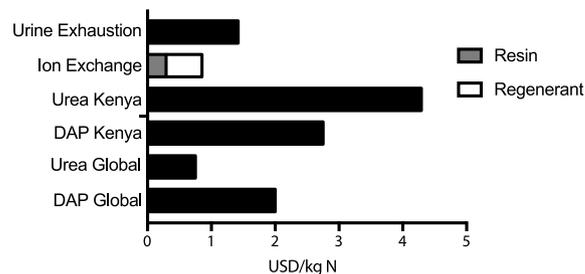


Fig. 5. Costs (USD/kg N) for urine exhaustion to wastewater treatment facility, ion exchange (resin and regenerant costs), and nitrogen fertilizer prices (in Kenya and globally).

costs. Regenerants other than sulfuric acid could improve the cost effectiveness of ion exchange, depending on whether low cost or high regeneration efficiency is more important in a given context. Compared to the $99.3 \pm 0.3\%$ regeneration efficiency of H₂SO₄, NaCl is 25 times cheaper than H₂SO₄ and has a regeneration efficiency of $77.4 \pm 5.5\%$; HCl is half the cost of H₂SO₄ and has a regeneration efficiency of $102 \pm 4.2\%$ (Kavvada et al., 2017; Tarpeh et al., 2018b). The placement of ion exchange within the Sanergy collection system could also influence urine processing costs. Loading urine containers at individual toilets with ion exchange resin and leaching the effluent could reduce collection frequency and thus collection costs, which are 30% of Sanergy's expenditures.

Ammonium sulfate produced from urine could be sold as a liquid fertilizer or added to solid fertilizer to make a premium Evergrow product. Based on crop-specific application rates, adding nitrogen to Evergrow could increase revenue by 31% for tomatoes and 58% for cabbage (Table S3, Section S1.6). The additional revenue generated from selling fertilizer could make nitrogen recovery from urine more profitable. While organic fertilizers are sorely needed to increase crop yields yet preserve soil quality, supply is low because domestic production is minimal (Shimeles et al., 2015). Urine-derived fertilizers are locally produced, avoiding large import transport costs that contribute as much as 40% markup for conventional fertilizers (Kenya Fertilizer Assessment, 2012). Producing ammonium sulfate from urine (\$0.85/kg N for Dowex Mac 3, 100 uses) is less expensive than government-subsidized prices for commercial fertilizers such as diammonium phosphate (\$2.75/kg N) and urea (\$4.29/kg N, see section S1.7). Resin and regenerant costs are lower than the global price of DAP but 13% higher than global urea prices (Fig. 5). Note that the costs of transporting urine from toilets was not included in these cost estimates, as this activity is already part of Sanergy's operations; however, it would need to be included for settings without existing excreta collection.

Other costs to consider for nitrogen recovery include facility space for regeneration and fertilizer production, as well as transport of ammonium sulfate to farmers. Partnerships with farm supply distributors could facilitate introduction of urine-derived fertilizers into existing

distribution channels. Several sub-Saharan African countries have higher fertilizer prices than Kenya (e.g., landlocked countries with higher transportation markups) (Shimeles et al., 2015), indicating even higher potential margins for urine-derived fertilizers. The volatility of synthetic fertilizer prices and their intermittent supply could make urine-derived fertilizers even more cost competitive. Fertigation may be a potential market segment for ammonium sulfate produced from urine because liquid fertilizers are easily incorporated into irrigation systems. Combining the value propositions of treating urine to meet discharge limits and produce fertilizer could improve the profitability for nitrogen recovery via ion exchange. Other high-value products, including industrial inputs (e.g., NH_4Cl , NH_4OH , microbially produced proteins (Pikaar et al., 2017)), could also be extracted from urine to improve financial viability.

3.6. Anaerobic digester effluent

Anaerobic digester effluent (digestate) is another underexploited waste stream from which ammonium could be recovered. In the Nairobi field site, Sanergy is currently exploring anaerobic digestion of feces at various scales to produce biogas, which produces an ammonia-rich liquid effluent (Table 1). In addition to producing ammonium sulfate fertilizer, removing ammonium from digestate reduces ammonium inhibition during microbial digestion of feces (Desloover et al., 2012). Similar to urine, the anaerobic digester effluent would need to be disposed of or treated before discharge. Recovering nitrogen from digestate could generate fertilizer products and reduce costs of digestate exhaustion. Ion exchange could be used to recover ammonium from digestate at various scales. In experiments conducted with digestate from Sanergy's anaerobic digesters treating feces, later breakthrough (~10 bed volumes) and a 25% lower adsorption density than urine were observed. The lower ammonium concentration in digestate compared to urine explains both later breakthrough and lower adsorption density. The slopes of normalized breakthrough curves in digestate and urine only differed by 2.5% (Fig. S4), indicating that longer run times or more resin would result in similar performance for digestate and urine.

4. Conclusions

In this study we evaluated the technical and financial feasibility of producing ammonium sulfate from urine using ion exchange. Ammonium breakthrough curves were reliably measured in Nairobi with Hach methods as an alternative to ion chromatography. Ten adsorption-regeneration cycles were performed without a decrease in performance, indicating Dowex Mac 3 could be used at least ten times before replacement. Adsorption density and regeneration efficiency were maintained at 65 L/d, a ten times larger setup than the 6.5 L/d representative of individual toilets. Based on urine composition, some nitrogen as ammonia was lost during the collection process; keeping storage tanks closed can reduce associated revenue losses. For implementation, process indicators such as effluent absorbance and electrical conductivity can be easily and cheaply measured. Based on resin and regenerant costs, ion exchange is less expensive than urine exhaustion and can produce a soil additive that is lower cost than commercial fertilizers in Nairobi. Future work includes evaluation and optimization of ion exchange for additional scales, geographical settings, and sanitation service provision schemes.

Notes

The authors declare no competing financial interests.

Declarations of interest

None.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.deveng.2018.07.002>.

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