ACS ES&T Engineering

pubs.acs.org/estengg

Article

Advancing the Design and Operating Conditions for Block Freeze Concentration of Urine-Derived Fertilizer

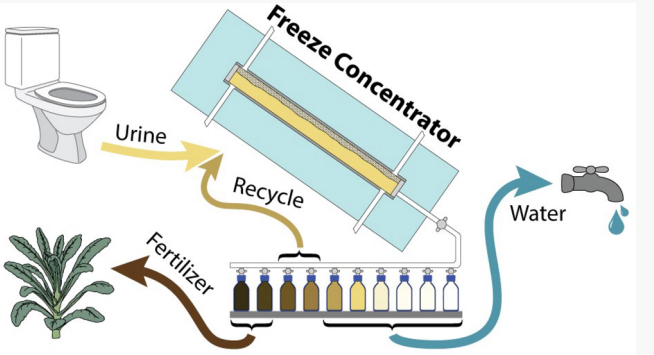
Abraham Noe-Hays,* Ryan John Homeyer, Arthur P. Davis, and Nancy G. Love

Cite This: https://doi.org/10.1021/acsestengg.1c00271

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: This paper is focused on evaluating the performance of a scalable block freezing device for concentrating aged, source-separated urine from a community-scale urine collection system that is used to create sustainable fertilizers. Temperature settings for two-stage freeze concentration were determined to be −6.5 °C during the first stage, −13 °C during the second stage, and 3.0−4.0 °C during the thaw stage. These temperatures reflect a smaller range than prior freeze concentration studies and have the potential to reduce energy consumption. The length of freeze and melt periods, the direction of heat transfer within the freeze chamber, and the orientation of the freeze chamber were varied to identify a preferred operating condition. The relative mass of nitrogen (N), phosphorus (P), and potassium (K) was constant during processing, and all were concentrated up to 3.3 times in a single stage with 80% nutrient retention. An iterative mass balance analysis of a two-stage system that incorporated recycling retained 92% of nutrients and achieved a concentration index of 5.8. This experimental concentrator reveals performance and unique operational features that elevate freeze concentration as a scalable option for urine separation systems.



KEYWORDS: *cryoconcentration, circular economy, nutrient recovery, wastewater, source separation*

INTRODUCTION

Nutrient pollution of surface water bodies causes harmful algal blooms that can threaten the viability of aquatic ecosystems and negatively impact human health.[1] It is estimated that 1.5 million metric tons of phosphorus (P) and 7.4 million metric tons of nitrogen (N) are deposited into surface water bodies globally every year.[2] Domestic wastewater is a major source of these nutrients, and urine (also called yellow water) contributes approximately 80, 50, and 70% of the N, P, and potassium (K) to domestic wastewater.[3,4]

While N and P in wastewater are causing damage to aquatic ecosystems and driving expensive upgrades in treatment, these same nutrients are in constant demand in agriculture. Nitrogen-based synthetic fertilizers formed using the Haber-Bosch process account for 1% of the world's total energy consumption.[5] Phosphate mining, while less energy-intensive than N production, depends on reserves that are distributed in a few countries.[6] The dependence of world agriculture on unevenly allocated nutrient resources leaves many countries reliant upon imports and vulnerable to dramatic price fluctuations[7] and geopolitical instability.

Widespread implementation of urine diversion (the collection of pure urine separate from the rest of the wastewater stream) can reduce nutrient pollution and produce a source for sustainable fertilizer production. Life cycle analysis of urine diversion has shown that it can have a reduced impact on the natural environment compared to conventional combined stream wastewater treatment.[8] Research has shown that people are receptive to the use of sustainable urine-derived fertilizers for food crops and nonfood plants once they learn about the benefits relative to other types of fertilizers, including synthetic and mined fertilizers that are used on most food crops.[9] However, when choosing techniques and equipment for the collection, transport, treatment, and distribution of urine and urine-derived fertilizers (UDFs), it is important to consider the energy and materials required to implement the various options, to ensure that these resource costs do not exceed that of conventional fertilizer production and wastewater treatment.

The concentration of plant nutrients is much higher in urine (0.9% N by mass) than in mixed wastewater (0.01% N by mass), but it is still much lower than in conventional agricultural fertilizers (30−46% N by mass).[10] Therefore,

Special Issue: Technology Baselines and Innovation Priorities for Water Treatment and Supply

Received: July 19, 2021
Revised: September 28, 2021
Accepted: September 29, 2021

concentrating the nutrients from urine into a reduced-volume product is an essential step in creating a urine-derived fertilizer that can offset production of its synthetic counterparts.[11] Volume reduction also reduces the energy required to transport urine-derived fertilizer[12] and reduces associated storage costs and labor for fertilizer application.

The volume of urine can be reduced either by removing water from the urine or by selectively removing nutrients from the urine. Others have investigated the second approach (with urine and with wastewater), to produce struvite, ammonium sulfate, or other ammonia compounds.[13,14] This paper focuses on the first approach, which results in a concentrated product containing all the urine nutrients and other constituents. Evaporation, reverse osmosis, and freeze concentration have all been demonstrated as methods for removing water from urine to increase the concentration of nutrients.[11,15−17] Forward osmosis membrane filtration[18] and ion exchange[19] have also been studied as methods to selectively remove ammonia from urine and wastewater streams; however, these technologies still reside primarily in the laboratory.

Despite the theoretical promise of these technologies, specific characteristics of urine complicate the use of both evaporation and reverse osmosis in practice. The predominant form of nitrogen in fresh human urine is urea, but the bacteria ubiquitous in urine collection pipes and storage tanks quickly hydrolyze it to ammonia/ammonium. Hydrolyzed source-separated human urine has a pH around 9,[20] which is close to the pK_a of ammonia (9.25).[2] Therefore, about half of the ammonia/ammonium in hydrolyzed urine is in the NH_3 form. Being small and uncharged, NH_3 is readily lost into the air during evaporation, and 20−30% is lost in reverse osmosis permeate.[11,15,21]

To overcome these issues, source separated urine must be pretreated before it can be effectively concentrated using either reverse osmosis or evaporation. This can be done by (1) preventing the initial conversion from urea to ammonia by either raising or lowering the pH to inactivate the urease enzyme,[17,20,22,23] (2) acidifying the stored urine to convert the ammonia to ammonium,[11,15,24] or (3) oxidizing the ammonia/ammonium to nitrate.[16] These treatment processes all add complexity to the processing system and require additional energy or chemical inputs. Furthermore, the achievable level of concentration using reverse osmosis is limited to about 5×, because as the osmolarity of the solution increases during the concentration process, so does the pressure required for further water extraction. Mineral scaling is also a consideration in reverse osmosis, though this may be manageable through the addition of additional antiscalant chemicals.[11]

In contrast, urine can be freeze-concentrated without pretreatment[25] and with good retention of ammonia.[26] In this process, urine is chilled below its freezing point, causing a portion of the water to freeze. The resulting ice is composed of pure water, leaving the solutes (nutrients, salts, and other constituents) dissolved in the smaller volume of remaining free water, raising the concentration of all solutes. The concentrated liquid is then separated from the pure ice, yielding a concentrated product. Lind et al.[25] demonstrated that 80% of the nutrients in urine could be concentrated into 25% of the original volume using block freezing methods. Gulyas et al.[26] tested falling film and stirred vessel methods and found that a three-stage process could yield a product about 4 times more concentrated than the original urine.

Freeze concentration techniques can be classified in four main categories: suspended crystallization, falling film, progressive, and block. The freeze concentration industry currently relies on the suspended crystallization method,[27] which can create viscous concentrates from feedstocks such as fruit juice, with final concentrations above 50° Brix (or 50 g of sucrose equivalent in 100 g of water). However, this technique involves complex and expensive equipment with separate components for producing seed ice crystals, growing the crystals, and then washing separated crystals.[28] Research into falling film and progressive freeze concentration is ongoing, with potential application in food processing for coffee and fruit juice concentrates.[29] Block freeze concentration has been investigated as an adjunct to falling film concentration in desalination[30] and fruit juice concentration.[29] However, block freezing has not yet gone beyond the laboratory, although its small number of moving parts makes it a particularly fruitful area of research due to lower associated production costs.[31] Additional advancements of associated equipment can make block freezing commercially viable, and it has been suggested that future freeze concentration research should be focused on developing new designs that incorporate the freezing and partitioning processes into a single apparatus.[32] Rane and Padiya[33] and Rane and Uphade[34] showed that the use of a low-lift heat pump with freeze concentration can lower energy consumption below that required by commercially available freeze concentration devices. Hybrid volume reduction processes have also been proposed, such as freeze concentration following reverse osmosis[32] and freeze concentration in conjunction with phosphorus precipitation.[35]

Freeze concentration has been demonstrated in small-scale laboratory experiments (100−750 mL)[25,26] to be effective for concentrating the nutrients in urine (including ammonia) without the addition of chemicals or other pretreatment. While this makes it an attractive alternative to membrane-based and evaporative processes, demonstration of a freeze concentration method that could be efficiently implemented at the building or community scale (processing thousands, not millions of liters per year) are lacking in the literature.

The objective of this study was to evaluate the performance of a novel block freezing device for the concentration of aged, source separated urine collected from the U.S.'s first community-scale urine collection system in Brattleboro, Vermont. We set out to (1) demonstrate scaled up performance relative to previous laboratory work, (2) utilize a freeze concentration method that is simpler than the conventional suspended crystallization technique, (3) demonstrate low energy intensity compared to evaporation, and (4) avoid the need for chemical pretreatment and the risk of fouling associated with membrane-based urine concentration methods. Our aim was to determine whether our device, which is much larger and uses different geometry than previously reported block freezing devices, could achieve similar or better fractionation of urine and higher final concentration levels than previous reports. Also, we evaluated the performance of our device using moderate freeze/thaw temperatures that are compatible with high-efficiency heat pumps. We compare the performance of our device to that of others reported in the literature, using metrics that include the level of concentration achieved, the differential between freezing and thawing temperatures, the amount of ice formed per volume of liquid treated, and the scalability of the concentrator architecture. The unit was designed to be mechanically and operationally

https://doi.org/10.1021/acsestengg.1c00271
ACS EST Engg. XXXX, XXX, XXX−XXX

simple, in comparison to suspended crystallization freeze concentrators, in order to minimize the expense and maximize the reliability of future deployments. The final operating conditions are identified and offer promise that an energy efficient, scaled-up system is possible.

MATERIALS AND METHODS

Freeze Concentrator Design. The freeze concentration apparatus used in these experiments (Figure 1) was constructed at the Rich Earth Institute Research Center in Brattleboro, VT, USA. The core of the apparatus was a flattened rectangular freeze chamber (interior dimensions 74 cm × 74 cm × 5 cm) that contained the urine as it froze and thawed. Two identical thermal transfer plates served as the two large (square) faces of the chamber, separated by four 5 cm tall acrylic perimeter walls. A single fill/drain port at the bottom of the freeze chamber allowed for liquid to be removed from and added to the chamber. The thermal transfer plates were hollow chambers through which a thermal transfer fluid circulated. Each plate consisted of two stainless steel sheets (thickness: 0.5 mm) separated by 6-mm-thick PVC spacers around the perimeter, forming an enclosed interior volume. The inlet and outlet of each plate were in opposite corners, and additional internal partitions ensured even flow throughout the entire volume. The entire freeze chamber was insulated with 10 cm of extruded polystyrene (Dupont Styrofoam XPS, R5/inch) and placed on a stand inclined 35°, 66°, or 75° from horizontal.

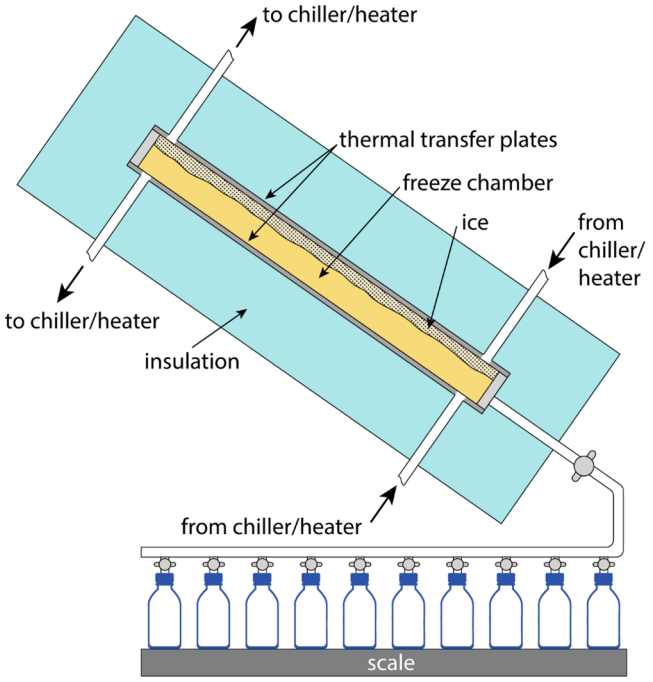


Figure 1. A side view of the freeze concentration apparatus used in this study. The apparatus was composed of a urine freezing chamber with thermal transfer panels on the large (square) faces and acrylic walls on the small (rectangular) faces. Coolant (with heat removed by a commercial chiller) was circulated through the thermal transfer panels to drive the freezing and melting of the ice block formed in the freeze chamber. The entire apparatus was insulated with polystyrene.

A water-based thermal transfer fluid of proprietary formulation was pumped from a reservoir, through the thermal transfer plates of the freeze chamber, and then back into the reservoir, using a 12 V DC centrifugal pump (Aubig Model DC40−1250). During the freezing phase, heat was removed from the reservoir via contact with chilled air by placing the reservoir inside a chest freezer (during preliminary singlet experiments) or by circulating the fluid through a small commercial chiller (Aqua Logic Inc. Model DS-5). During the thaw phase, heat was added to the reservoir using an aquarium heater (100−200W). The duty cycles of the chest freezer, chiller, and heater were all controlled by an Arduino Mega microcontroller, based on temperature data from digital temperature probes (Dallas Semiconductor DS18b20), to maintain the fluid at the target temperature. The chiller was not optimized for load or operating temperature, and such optimization is considered a future phase of the work.

Freeze Concentrator Operation. Urine used in these experiments was obtained from urine-collecting portable toilets at public events in western MA and southern VT as part of the Rich Earth Institute's Urine Nutrient Reclamation Program (UNRP) and represents the aggregated urine of >1000 people. All urine used was pasteurized by heating it to a temperature of 80 °C for 90 s, in compliance with the Rich Earth Institute's solid waste management permit from the State of Vermont. Two batches of urine were used as feedstock for the freeze trials. Feedstock A contained 7.22 g/L N, 0.548 g/L P, 2.044 g/L K, and 14.31 ± 0.65 g/L TDS and had a freezing point depression of −1.76 °C. Feedstock B contained 5.1 g/L N, 0.289 g/L P, 1.608 g/L K, and 12.35 ± 0.93 g/L TDS and had a freezing point depression of −1.46 °C. These nutrient concentrations are higher than some values reported in the literature for stored urine,[36] but they are similar to those used in other experiments involving hydrolyzed urine.[18,37] See Table S2 for the reference to which feedstock was used in each trial.

Nine single experiments (#1 through #9) were processed through stage 1 only (processing untreated hydrolyzed urine) and were conducted to both establish operating conditions and verify performance. Triplicate experiments were conducted for stage 1 and stage 2 (preconcentrated urine) to demonstrate levels of nutrient concentration that could be achieved and the purity of the reject water. Each experimental run of the freeze concentrator consisted of two phases: freezing and fractional melting. To initiate the freezing phase, 20 L of feedstock urine (stored, hydrolyzed urine) was pumped into the freeze chamber through the bottom port. Chilled thermal transfer fluid was circulated (~21−35 mL/s) through the upper thermal transfer plate to absorb heat from the urine in the freeze chamber. Cooling was performed through the top plate exclusively so that ice formation would begin along the top of the chamber. We expected, based on prior experiments, that as ice formed and excluded nutrient salts represented as TDS, the concentration gradient between this more concentrated solution and the less dense bulk solution would drive convective mixing of the chamber contents, reducing entrapment of newly concentrated urine within the advancing ice front. Chilling continued until a temperature sensor located in the bottom center of the urine chamber reached the target temperatures, which were −6.5 °C and −13 °C for the stage 1 and stage 2 experiments, respectively.

Operating conditions that were varied in the single experiments were the orientation of the freeze chamber, the length of the freezing and melting periods, and the direction of heat transfer within the freeze chamber. The operating conditions that were used during the triplicate experiments were a freeze chamber orientation of 35°, heat transfer driven

https://doi.org/10.1021/acsestengg.1c00271
ACS EST Engg. XXXX, XXX, XXX−XXX

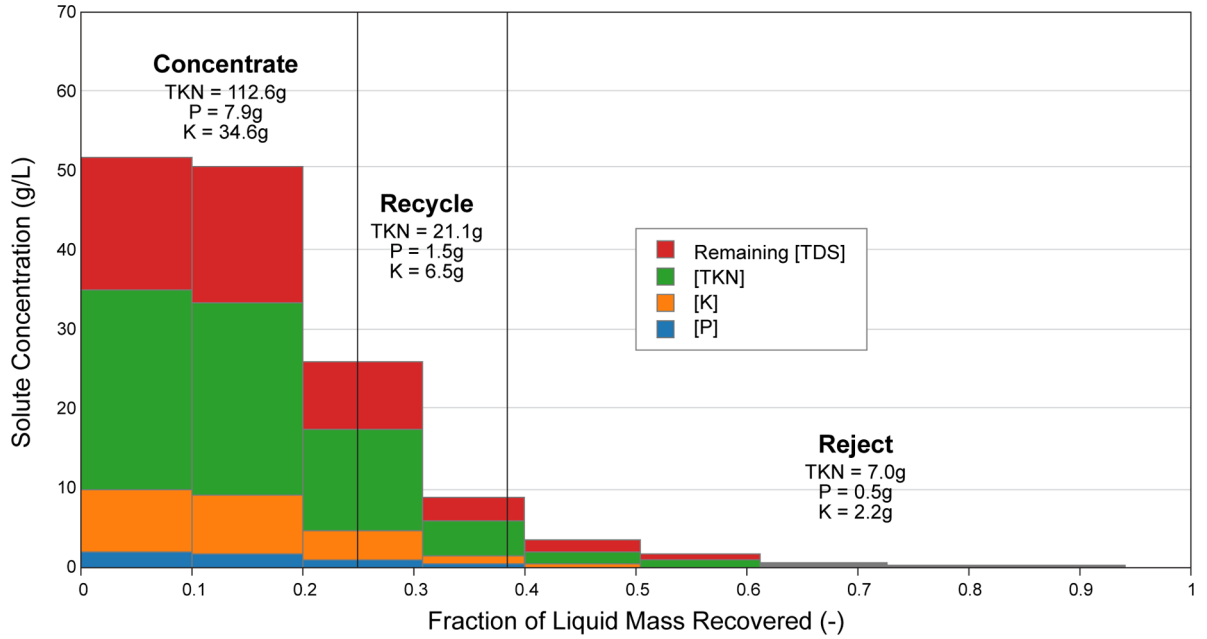


Figure 2. Concentration (g/L) of nutrients in the liquid fraction of each of the 10 collection vessels from single experiment #7 plotted against the fraction of the total liquid mass that each collection vessel contained. The solute concentration of feedstock A used in this experiment is provided in Table S3.

by the top plate during the freezing period, heat transfer driven by both the top and bottom plates during the melting period, and approximate freezing and melting periods of 30 h each.

The fractional melting phase was initiated by turning off the chiller or chest freezer. A valve in the fill/drain line was opened, and free liquid urine concentrate flowed into a distribution manifold connected by hoses to a set of 10 collection vessels. The 10 vessels were used for research purposes to track progress of the freeze concentrator and verify its performance. The vessels rested on a lab-built weighing platform, which relayed the approximate weight of the combined contents of all the vessels to the Arduino controller. The controller activated electric valves at 2 kg intervals, sequentially and evenly partitioning the output of the concentrator into the 10 vessels. Melting was facilitated by using the Arduino controller to run the heater as needed to maintain the thermal fluid at a temperature at least 3 °C warmer than the ice temperature probe, but no higher than 4 °C. Toward the end of each run, the thermal fluid temperature exceeded 4 °C due to passive heat gain from the environment as well as reduced contact between the shrinking ice block and the thermal transfer plates, accompanied by a reduction in melting rate; however, this did not occur until about 75% of the liquid and over 98% of TDS had been recovered. The melting period was defined as the time taken for the first 75% of the liquid to be recovered. During the melting phase of all trials, the thermal fluid was circulated through the bottom plate, and in single experiment #9 and the triplicate experiments, it was simultaneously circulated (~28−45 mL/s) through the top plate as well.

Physical Analysis. The electrical conductivity (EC) and mass of each of the 10 meltwater fractions was measured in the Rich Earth Institute's laboratory. EC was measured using a direct conductivity probe (Hach CDC401), and masses were measured using a digital scale (Mettler Toledo, New Classic MF). Because the relationship between EC and ionic concentration is not linear, a set of serial dilutions of concentrated urine was performed to calculate a quadratic relationship between EC and ionic concentration. Ionic concentration is expressed using a solute concentration factor, which is relative to the concentration (w/w) of a urine−water solution with an EC of 1 mS/cm (see SI.2 for details).

The feedstocks used for the entire suite of experiments presented in this paper, as well as the 10 fractions from single experiment #7, were analyzed for plant nutrients by the University of Maine's Analytical Lab and Maine Soil Testing Service. Total Kjeldahl nitrogen (TKN) was measured by Micro Kjeldahl Analysis using a block digester. Soluble P and K were measured using a Spectro model Genesis radial view ICP-OES, and ammonium-N was measured following Method 4500-NH3 G from Standard Methods for the Examination of Water & Wastewater.[38]

The TDS of the feedstocks were measured by evaporating water from samples in an oven (QL Model 10 Oven) at 104 °C and measuring the change in sample mass. Because ammonia and carbonate are both subject to volatilization, and the concentration of ammonia was already known while that of carbonate was not, sodium hydroxide was added to the urine and mixed by swirling before drying to raise the pH and retain the carbonate while driving off the ammonia. The mass of added NaOH was then subtracted and the mass of volatilized ammonia (calculated based on previous ammonia analysis) added to arrive at the reported TDS values.

Data Analysis. The liquid fractions from each run were characterized using two metrics: mass fraction (MF_n) and concentration index (CI). MF_n is defined as the fraction of the total liquid mass that contains the first n% of dissolved solids recovered during the fractional melting process. MF_n is calculated using linear interpolation to find the fraction of the total liquid mass that corresponds to a dissolved solids recovery of n% (see SI.3 for calculation procedure). CI, expressed in eq 1, is defined as the ratio of the fraction of total solids recovered to the fraction of the total liquid mass into which the solids have been concentrated.

https://doi.org/10.1021/acsestengg.1c00271
ACS EST Engg. XXXX, XXX, XXX−XXX

Table 1. Results of the Three Replicated Trials for the Stage 1 and Stage 2 Block Freeze Concentration of Hydrolyzed Human Urine Based on Measured EC Values and Calculated SCF, as Described in Supporting Information section SI.3[a]

	stage 1		stage 2	
fraction	mass fraction	concentration index	mass fraction	concentration index
feedstock	1	1	1	3.30
concentrate (MF_{80})	0.24 ± 0.0098	3.30	0.40 ± 0.014	6.67
stage 1 recycle (MF_{95}–MF_{80})	0.19 ± 0.0073	0.77		
stage 2 recycle 2 (MF_{95}–MF_{80})			0.20 ± 0.012	2.41
stage 2 recycle 1 (MF_{98}–MF_{95})			0.13 ± 0.0089	0.73
reject (MF_{100}–MF_{95})	0.56 ± 0.014	0.09		
reject (MF_{100}–MF_{98})			0.27 ± 0.013	0.24

[a]The mass fractions reported are the mean values achieved for each fraction: concentrate (80% of total solids recovered), recycle from stage 1 or recycle 2 from stage 2 (the subsequent 15% of total solids recovered), recycle 1 from stage 2 (the subsequent 3% of total solids recovered), and reject (the remaining 5% of total solids recovered for stage 1 or 2% for stage 2). Uncertainties reported are the standard deviation from the mean value. Calculations are shown in section SI.3.

$$\mathrm{CI} = \frac{n\%}{\mathrm{MF}_n} \quad (1)$$

All calculations and visualizations were made using Microsoft Excel and RStudio. Uncertainty, when provided, is presented as mean ± standard deviation.

RESULTS

Distribution of Nutrient Recovery Across Fractions. During the melting phase of each freeze/thaw cycle, the conductivity and TDS concentration of the liquid draining from the concentrator progressively decreased as the melt progressed. The first, most concentrated liquid was designated as the concentrated product fraction (MF_{80}) and contained 80% of all recovered TDS. The next fraction was designated as the recycle fraction, so named because its TDS concentration was similar to that of the feedstock used in that freeze/thaw cycle, making it suitable for recycling into the feedstock of the next cycle. The final fraction was designated as the reject fraction because it was much more dilute than the original urine, and this fraction can be discharged as waste or used as influent for a subsequent water recovery process. Cutoff metrics for the recycle and reject fractions differed slightly between stage 1 and stage 2 experiments. Following the concentrated fraction, the recycle fraction from stage 1 and stage 2 contained the next 15% (MF_{95} − MF_{80}) and 18% (MF_{98} − MF80) of recovered TDS, respectively. The recycle fraction for stage 2 runs was broken into two subsets: a more concentrated fraction that would be recycled into the second stage process, recycle 2 (MF_{95} − MF_{80}), and a less concentrated fraction that would be recycled into the single stage process, recycle 1 (MF_{98} − MF_{95}). The reject fraction contained the last 5% and 2% of recovered solids in stage 1 and stage 2 experiments, respectively. We chose those cutoffs for the reject fraction as a compromise between removing water and retaining nutrients. A different cutoff point might be chosen depending on the priorities of the operator.

The contents of the 10 serial collection vessels that were collected during single experiment #7 (Feedstock A) were analyzed for TKN, ammonia/ammonium-N, soluble P, soluble K, and TDS, with results shown in Figure 2. While the absolute concentration of nutrients varied greatly between vessels, the ratio of nutrients within each vessel was consistent and indicates that N, P, and K were all concentrated to a similar extent (see Figures S4 and S5). The result is a concentrated nutrient solution with the same profile as the original urine, rather than separate products containing the different constituent nutrients. Freeze concentration can be partnered with other technologies that remove trace contaminants, address odor, or separate the nutrient constituents. For instance, freeze concentration can be used after struvite precipitation,[35] as part of a multistep process that produces multiple products.

The water that is rejected from our two-stage system contains 8% of the total influent nutrients and is 10% of the concentration of the feedstock urine. This reject water (580 mg/L N; 44 mg/L P) has a higher nutrient content than residential wastewater (26−75 mg/L N; 6−12 mg/L P),[39] but an extremely low volume, estimated at 1 L/person/day. Given that 80% of the N and 50% of the P in domestic wastewater comes from urine,[3,4] and our freeze concentration system recovers 92% of both nutrients, the N and P levels in domestic wastewater could be reduced by 74% and 46%, respectively, by diverting urine to our freeze concentrator and then directing the reject water to the building's wastewater system. This could facilitate simplified or downscaled centralized or onsite treatment that can focus more on carbon sequestration and carbon-based resource recovery or water reuse. If a lower-strength reject water is required, a small increase in the size of the recycle fraction would result in a large reduction in the solutes included in the reject fraction (see Figure 2).

Concentration Levels Achieved. The triplicate concentration runs were conducted using unconcentrated, hydrolyzed urine applied to stage 1 (EC = 36.2 mS/cm, SCF = 40.9, freezing point depression = −1.46 °C). The mass fractions and concentration indices are given in Table 1. A separate set of triplicate runs was conducted to simulate a stage 2 scenario that received a concentrated feedstock prepared from the pooled product of all previous trials and pretrials. This pooled concentrate was diluted with distilled water to adjust its concentration to match that of the MF_{80} (concentrate) fraction from the stage 1 trials (EC = 98.9mS/cm, SCF = 134.9, freezing point depression = −5.94 °C). The mass fractions and concentration indices are given in Table 1. The results show that using a two-stage approach to concentration allowed nearly 7× the concentration, with the second stage doubling the level of concentration from the first stage. The recycle streams return to a feed stream that is more concentrated and, therefore, have the impact of diluting feed streams to stage 1 and 2 to a small degree.

An iterative mass balance model of an integrated two-stage concentration system was developed, with inter- and intrastage

https://doi.org/10.1021/acsestengg.1c00271
ACS EST Engg. XXXX, XXX, XXX−XXX

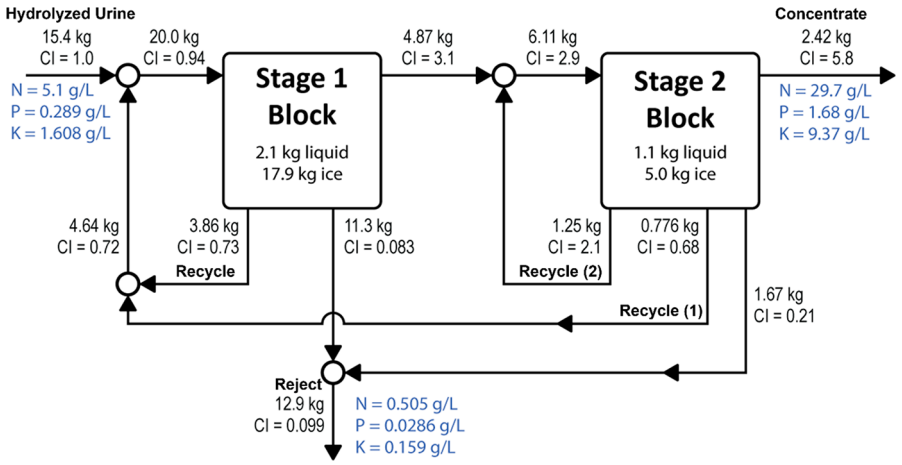


Figure 3. A mass balance flow diagram displaying the steady state concentration levels predicted by an iterative mass balance model for field operation of a two-stage block freeze concentration process. Nutrient concentrations are displayed for the process feedstock (hydrolyzed human urine), the concentrated effluent from the second stage concentration, and the reject water. The masses (kg) of free liquid and ice formed during each process are also displayed.

recycling of the intermediate-concentration (recycle) fractions from each stage. The model was initialized using feedstock concentration indices of 1 for the first stage and 3.3 for the second stage, and outputs from each stage were calculated using MF_{80} and MF_{95} values determined in the first-stage trials and MF_{80}, MF_{95}, and MF_{98} values from the second-stage trials. These outputs were used to recalculate the inputs to both stages, following the connections in the flow diagram. Iterations continued until the model converged, and outputs are shown in Figure 3. Concentration index (CI) values are in reference to the hydrolyzed, pasteurized urine feedstock, which is defined as having a CI of 1. Results from this modeling effort produced a product with a concentration index (5.8) near what was experimentally determined and reported in Table 1 (6.7).

Creating Conductivity Monitoring Protocol. The relative concentrations of solute in the liquid fractions produced in each trial were determined using electrical conductivity (EC) measurements. A urine solution with an EC of 124.8 mS/cm (feedstock A, concentrated sample) was serially diluted (~1:1) with distilled water to create a series of samples, each sample containing a known mass of the original source solution and a known mass of added water. The EC of the final sample in this series measured <1 mS/cm. For each sample, we measured EC and calculated the relative solute content (mass basis) in reference to the first (most concentrated) sample. We found that EC varied nonlinearly with solute concentration, and a quadratic polynomial was fitted to these data ($r^2 > 0.99$). This function was then normalized onto a new solute concentration factor (SCF) scale (eq 2), such that a sample with an EC of 1 mS/cm had an SCF value of 1 (derived in section S2). Values for γ and δ were 0.00366 and 0.996, respectively.

$$\mathrm{SCF(EC)} = \gamma(\mathrm{EC}^2) + \delta(\mathrm{EC}) \quad (2)$$

Three additional sets of serially diluted samples were prepared from different batches of urine to test the agreement of their individual SCF curves with eq 2. These samples had electrical conductivities of 18.3 (diluted product produced from feedstock A), 36.2 (feedstock B), and 111.3 (concentrated product produced from feedstock B) mS/cm. SCF functions were determined for these samples with the method described above and plotted together to check for agreement (Figure S2). The maximum absolute difference (equation S3) between the SCF predicted by eq 2 and the SCF predicted by the curve for a given sample was 2.18 SCF (5.1%; Table S1). The maximum percent difference (equation S4) between the SCF predicted by eq 2 and the SCF predicted by the curve for a given sample was 7.4% (1.56 SCF; Table S1). This shows that SCF can be used to relate the amount of solute in a given urine solution to other urine solutions collected during the fractional melting portion of a run as well as to the urine solution that is initially fed into the freeze concentrator. The relationship between SCF and electrical conductivity allows for the effectiveness of the freeze concentrator to be understood with a single laboratory measurement for urine from various sources and with differing concentration indices.

Selection of Operational Parameters. The nine single experiments were conducted with varying operational parameters to identify a configuration for use during the subsequent runs. These experiments were designed to identify conditions that minimized cycle time while meeting the following fractionation metrics: the first 30% of recovered mass having >80% of recovered solutes, and the last 50% of recovered mass having <5% of recovered solutes. Variables included the length of the freeze and melt periods, the direction of heat transfer within the freeze chamber, and the orientation of the freeze chamber (described in SI.3). Freezing periods between 27.3 and 109 h and melting periods between 14.6 and 36.0 h all met our fractionation metrics. Freezing and melting from opposite directions improved the degree of fractionation. Melting was more rapid when heat was applied from below as opposed to above, due to the continuous contact between the ice block and the lower plate throughout the melting process. Inclination of the chamber at 35° and 66° from the horizontal maintained that contact well, while inclination at 75° did not. Rotating the freeze chamber 45° between diamond orientation (drain at the bottom point of the diamond) and square configuration (drain in one of the two bottom corners) had no discernible effect. On the basis of this series of experiments, the triplicate runs were performed using a 35° inclination, freezing and thawing periods of approximately 30 h each, circulation of cooling fluid through the upper plate only during the freeze phase, and circulation of warming fluid through both the upper and lower plates during the melt phase.

https://doi.org/10.1021/acsestengg.1c00271
ACS EST Engg. XXXX, XXX, XXX−XXX

Working Fluid Temperatures. Target temperatures for the heat transfer working fluid used in these experiments were −6.5 °C during the freezing phase of the first-stage concentration trials, −13 °C during the freezing phase of the second-stage trial, and 3.0−4.0 °C during the thaw phase of all trials. These set points yielded a temperature differential of 9.5−10.5 °C between the working fluid target temperatures in the freezing and thawing phases for stage 1 concentration and 17 °C for stage 2 concentration. The colder set point was needed for stage 2 due to the lower freezing point of the preconcentrated feedstock (−5.94 °C) compared to the unconcentrated urine used in stage 1 (−1.46 °C). The set point for freezing was chosen because it allowed a portion of the concentrate fraction to remain unfrozen (see discussion on ice mass), while the melting temperature set point was chosen to produce a melt period roughly equal in length to the freeze period.

Mass of Ice Formed. Partial freezing occurred in the concentrator, which enhanced the efficiency of the system compared to complete block freezing. At the end of the freezing phase during the triplicate stage 1 and stage 2 experiments, unfrozen concentrate (averaging 2.1 and 3.8 kg, respectively) drained freely from the apparatus when the drain was opened. The mass of ice formed during the freeze phase was 10−19% less than the total feedstock mass and therefore required proportionately less heat removal than would have been required if the urine were completely frozen. Complete freezing would also have required a lower freezing temperature, which has undesirable energy implications.

DISCUSSION

Block Freezing of Urine Achieves High Concentrations Using a Simple and Scalable Process. Using a block-freeze concentrator to process pasteurized stored urine, we produced a first-stage concentrate that retained 80% of the TDS from the urine in less than 25% of the original urine mass, for a concentration index of 3.3. Subsequent second-stage concentration (using the concentrate from the first stage as a feedstock) yielded a product containing 80% of the TDS from the feedstock in 40% of the feedstock mass, with a concentration factor of 2.0 within the stage, and 6.7 across both stages. A model integrating the two stages (and including reincorporation of the recycle fraction) predicted a final product concentration index of 5.8, with 92% of solids retained in the concentrate and 8% lost in the reject fraction. This two-stage block process achieves a higher concentration index than a six-stage falling film process for concentrating fruit juice (CI = 4.0)[29] or a five-stage falling film process for desalinating seawater (CI = 3.8).[30]

The flat plate design of our freeze concentrator is fundamental to its scalability and represents a significant advance in design. The rate of heat removal and ice formation in a block freeze concentrator is influenced by the surface area of the chilled walls, the temperature of the coolant, and the thickness of the ice block. If the area of the chilled wall is increased while the coolant temperature and ice thickness are kept constant, we anticipate that the processing capacity of the freeze concentrator will scale up in proportion to the area of the chilled wall, with little change in performance. Block freezing devices previously reported in the literature scale poorly because they are cylindrical,[25,30,35] resulting in dramatic reductions in surface-area-to-volume ratio if they are scaled in more than one dimension. Our design can scale up while maintaining a constant surface-area-to-volume ratio by (1) enlarging the thermal transfer plates along both dimensions while keeping the spacing between the plates constant and (2) creating a stacked array of alternating thermal transfer plates and freeze chambers, like a multilevel sandwich. These strategies can be combined for greater capacity.

A major benefit of block freezing compared to conventional suspended crystallization is the simplicity of the process. Suspended crystallization requires a highly engineered system with carefully monitored process conditions, in which seed crystals are formed in one chamber, ripened in another, and washed in a third.[31] In block freezing, liquid is frozen in a single process step and then fractionally melted in the same chamber. The experimental apparatus described in this paper may appear complex due to the 10-vessel sampling system, which included a weighing platform and many valves. In a practical implementation, this could be simplified to a motorized three-output manifold, with transitions in valve position based on the temperature of the remaining ice and conductivity of the liquid draining from the concentrator.

Less Refreezing Results in Higher Efficiency. In freeze concentration, some intermediate-concentration meltwater is typically recycled and frozen more than once, which can add substantially to energy consumption. The ratio of the mass of water removed to the mass of ice produced is a key factor in total energy use. Compared with a system modeled by Pazmiño et al.[29] that combined six stages of falling film and one of block freezing to concentrate fruit juice, our two-stage system required the formation of only one-third as much ice per kilogram of water removed (1.8 vs 5.5 kg ice produced/kg water removed). Consequently, our two-stage block freeze concentration system will require less energy to achieve the same level of nutrient concentration.

Moderate Working Temperatures and Latent Heat Recovery Could Reduce Energy Demand to Levels Competitive with Reverse Osmosis and Evaporation. Our block freezing process for concentrating urine achieved better partitioning of TDS than did other block freezing methods reported for fruit juice or seawater, likely due to more moderate temperatures of the thermal transfer fluid during the freezing and melting phases of our experiment (−6.5 °C and ≤4 °C, respectively). The fraction of recovered TDS in the first 40% of recovered liquid was 95% in our triplicate stage 1 trial using hydrolyzed human urine (1.2% TDS), compared to only about 70% using 1.7−3.2% salt solution[30] and <80% with 0.9% sucrose solution.[29] This is likely due to the much lower freezing temperatures (−20 °C and −10 °C, respectively) and higher melting temperatures (40 and 20 °C, respectively) used in those trials, which may have caused greater solute inclusion in the ice due to rapid freezing, and rapid selective melting of ice in contact with the chamber wall. Similarly, frozen urine partially thawed in a 30−40 °C bath achieved only 60% solute recovery in the first 40% of recovered liquid,[35] while frozen urine slowly melted through contact with room temperature air (no values given for time or temperature) achieved 80% solute recovery in the first 25% of recovered liquid.[25]

More moderate working temperatures also require less energy for pumping heat. Efficient refrigeration systems can move considerably more energy than they consume, expressed as a coefficient of performance (COP) > 1. A system that consumes 1 W of electricity to remove 1 W of heat has a COP of 1. The theoretical maximum COP of a refrigeration system, as determined by Carnot's theorem, is $Temp_{Cold}/(Temp_{Hot} -$

https://doi.org/10.1021/acsestengg.1c00271
ACS EST Engg. XXXX, XXX, XXX−XXX

$Temp_{Cold}$).[40] The efficiency of freeze concentration therefore increases if the compressor and evaporator temperatures can be reduced. This can be done through latent heat recovery, by using melting ice as a sink for the heat that is being removed to simultaneously create ice elsewhere in the system, a common practice in freeze concentration. Calculated COP values of 9[29] and 7.9[30] are reported for a 15 and 20 °C temperature differential, respectively, between compressor and evaporator temperatures, using realistic efficiency values for modern heat pumps. The temperature differential between our freezing and melting temperatures is 10.5 °C in the first stage and 17 °C in the second stage, so if thermal resistance between the heat pump and working fluid can be minimized, COP values near 9 and 8 are achievable for the two-stage concept introduced here.

The formation of 1 kg of ice requires the removal of 334 kJ (92.8 Wh) of heat,[41] which would consume 39 kJ (11 Wh) of electricity if performed using a heat pump with a COP of 8.5. The system in this study extracted 0.77 kg of reject water per kilogram of ice formed, resulting in a calculated electricity demand of 14 Wh/kg water removed. Additional energy would be required for other cooling loads, including thermal cycling and removal of intruding ambient heat, but ice formation accounted for 80% of cooling demand in a freeze concentration analysis by Rane and Uphade.[34] Therefore, the energy required for ice formation is a good approximation of the total energy demand for the entire process.

This estimate is substantially lower than the energy requirement reported by Gulyas et al.[26] for the energy consumption specifications of freeze concentrators capable of achieving a concentration index of four. A unit removing 250 L/h (suitable for a community of 5,840 people) would consume 244 Wh/kg water removed, while a 25 000 L/h model (for a community of 584,000) would consume 30 Wh/kg. Concentrating urine through evaporation requires 110−710 Wh/L, depending on the extent of heat recovery,[16] while reverse osmosis requires 8−12 Wh/L, depending on whether the influent is preheated.[24] Two-stage block freeze concentration therefore has the potential to use much less energy than evaporation and slightly more energy than reverse osmosis, with the additional benefit of no chemical or energy usage for pretreatment of the urine before concentration.

EC Monitoring Facilitates Automation. Successful implementation of block freeze concentration as a technique for recovering nutrients from urine will require a method for sorting the resulting meltwater stream into the concentrate, recycle, and reject fractions. EC is shown here to be a reliable measurement for accurately discerning the relative concentration of the plant nutrients N, P, and K. Automated separation of the fractions could be accomplished using a system that monitors the EC of the concentrator effluent, compares that level to targets, and actuates valves or pumps accordingly. EC monitoring will help to ensure consistent composition of concentrated urine products batch-to-batch, a necessary element of a commercializable design.

ENGINEERING CONTEXT

The traditional approach used to manage nutrients at centralized water resource recovery facilities (WRRFs) is to collect the concentrated N, P, and K nutrients that are present in human urine (0.8 to 2 L discharged per person per day) as a mixture with feces and dilution water (30 to 130 L discharged per person per day) and convey them to the WRRF where various technologies are applied, along with input energy and chemical resources, to transform or reconcentrate the incoming nutrients. In the U.S., WRRFs only recover 21% P and 11% N,[42] mostly in the form of biosolids. The transportation costs to haul these nutrients to where they are needed as well as the operational costs of the technologies used to process the nutrients for reuse reflect embedded energy that makes those nutrients less environmentally sustainable.[8] With urine separation, concentration technologies start with N, P, and K levels much higher than they do with resource recovery technologies applied at centralized WRRFs. Here, we showed that freeze concentration is a viable approach to achieving at least 6× concentration of nutrients from human urine that was collected at the source and not diluted with flush water. Concentration reduces the cost of transporting nutrients to farms and can help to create a pathway for the sustainable development of a new generation of sustainable fertilizers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestengg.1c00271.

Summaries of each trial conducted, methods of calculation for experimental parameters, and details regarding model assumptions/calculations (PDF)

AUTHOR INFORMATION

Corresponding Author

Abraham Noe-Hays − *Rich Earth Institute, Brattleboro, Vermont 05301, United States;* orcid.org/0000-0002-8592-9817; Email: abe@richearthinstitute.org

Authors

Ryan John Homeyer − *Rich Earth Institute, Brattleboro, Vermont 05301, United States;* orcid.org/0000-0002-9644-1569

Arthur P. Davis − *Rich Earth Institute, Brattleboro, Vermont 05301, United States*

Nancy G. Love − *University of Michigan, Ann Arbor, Michigan 48109-2125, United States;* orcid.org/0000-0002-9184-2451

Complete contact information is available at: https://pubs.acs.org/10.1021/acsestengg.1c00271

Notes

The authors declare the following competing financial interest(s): In addition to employment at the Rich Earth Institute, Abraham and Arthur are also employed at Rich Earth LLC, a spinoff that is working to commercialize urine treatment technologies.

ACKNOWLEDGMENTS

This research was supported by the U.S. National Science Foundation under award numbers INFEWS 1639244. We acknowledge the contributions of Jesse Fox, Lucas Raimondi, Kedar Aparadh, Cole Teranes, Abigail Rae-Cohen, Yen Je Ooi, Alex Sabido, and James Eraci to this research.

REFERENCES

(1) Sutton, M. A.; Bleeker, A.; Howard, C. M.; Bekunda, M.; Grizzetti, B.; de Vries, W.; van Grinsven, H. J. M.; Abrol, Y. P.; Adhya, T. K.; Billen, G.; Davidson, E. A.; Datta, A.; Diaz, R.; Erisman, J. W.; Liu, X. J.; Oenema, O.; Palm, C.; Raghuram, N.; Reis, S.; Scholz, R.

W.; Sims, T.; Westhoek, H.; Zhang, F. S.; Ayyappan, S.; Bouwman, A. F.; Bustamante, M.; Fowler, D.; Galloway, J. N.; Gavito, M. E.; Garnier, J.; Greenwood, S.; Hellums, D. T.; Holland, M.; Hoysall, C.; Jaramillo, V. J.; Klimont, Z.; Ometto, J. P.; Pathak, H.; Plocq, F. V.; Powlson, D.; Ramakrishna, K.; Roy, A.; Sanders, K.; Sharma, C.; Singh, B.; Singh, U.; Yan, X. Y.; Zhang, Y. Our Nutrient World: The challenge to produce more food and energy with less pollution. *Global Overview of Nutrient Management on behalf of the Global Partnership on Nutrient Management and the International Nitrogen Initiative*; Centre for Ecology and Hydrology, Edinburgh, 2013. http://nora.nerc.ac.uk/id/eprint/500700/ (accessed June 25, 2021).

(2) Randall, D. G.; Naidoo, V. Urine: The liquid gold of wastewater. *J. Environ. Chem. Eng.* **2018**, *6* (2), 2627−2635.

(3) Larsen, T. A.; Alder, A. C.; Eggen, R. I. L.; Maurer, M.; Lienert, J. Source separation: Will we see a paradigm shift in wastewater handling? *Environ. Sci. Technol.* **2009**, *43*, 6121−6125.

(4) Friedler, E.; Butler, D.; Alfiya, Y. Wastewater composition. In *Source Separation and Decentralization for Wastewater Management*; Larsen, T. A., Udert, K. M., Lienert, J., Eds.; IWA Publishing, 2013; pp 241−257.

(5) U.S. Department of Energy, Office of Science. Sustainable Ammonia Synthesis: Exploring the scientific challenges associated with discovering alternative, sustainable processes for ammonia production, last revised February 18, 2016. https://www.osti.gov/biblio/1283146-sustainable-ammonia-synthesis-exploring-scientific-challenges-associated-discovering-alternative-sustainable-processes-ammonia-production (accessed July 12, 2021).

(6) U.S. Geological Survey. Mineral commodity summaries 2021: U.S. Geological Survey. DOI: 10.3133/mcs2021 (accessed July 14, 2021).

(7) Huang, W.-Y.; McBride, W.; Vasavada, U. Recent volatility in U.S. fertilizer prices: Causes and consequences. *Amber Waves.* **2009**, *7* (1), 4.

(8) Hilton, S. P.; Keoleian, G. A.; Daigger, G. T.; Zhou, B.; Love, N. G. Life Cycle Assessment of Urine Diversion and Conversion to Fertilizer Products at the City Scale. *Environ. Sci. Technol.* **2021**, *55* (1), 593−603.

(9) Segre Cohen, A.; Love, N. G.; Nace, K. K.; Arvai, J. Consumers' acceptance of agricultural fertilizers derived from diverted and recycled human urine. *Environ. Sci. Technol.* **2020**, *54* (8), 5297−5305.

(10) Martin, T. M. P.; Esculier, F.; Levavasseur, F.; Houot, S. Human urine-based fertilizers: A review. *Crit. Rev. Environ. Sci. Technol.* **2020**, 1.

(11) Maurer, M.; Pronk, W.; Larsen, T. Treatment processes for source-separated urine. *Water Res.* **2006**, *40* (17), 3151−3166.

(12) Medeiros, D. L.; Kiperstok, A. C.; Nascimento, A.; Cohim, E. H. B.; Kiperstok, A. Human urine management in resource-based sanitation: water-energy-nutrient nexus, energy demand and economic performance. *Sustainable Production and Consumption.* **2021**, *26*, 988−998.

(13) Simha, P.; Ganesapillai, M. Ecological Sanitation and nutrient recovery from human urine: How far have we come? A review. *Sustainable Environment Research.* **2017**, *27* (3), 107−116.

(14) Kogler, A.; Farmer, M.; Simon, J. A.; Tilmans, S.; Wells, G. F.; Tarpeh, W. A. Systematic Evaluation of Emerging Wastewater Nutrient Removal and Recovery Technologies to Inform Practice and Advance Resource Efficiency. *ACS ES&T Engineering* **2021**, *1* (4), 662−684.

(15) Ray, H.; Perreault, F.; Boyer, T. Rejection of nitrogen species in real fresh and hydrolyzed human urine by reverse osmosis and nanofiltration. *J. Environ. Chem. Eng.* **2020**, *8* (4), 103993.

(16) Udert, K. M.; Wächter, M. Complete nutrient recovery from source-separated urine by nitrification and distillation. *Water Res.* **2012**, *46* (1), 453−464.

(17) Senecal, J.; Vinnerås, B. Urea stabilisation and concentration for urine-diverting dry toilets: Urine dehydration in ash. *Sci. Total Environ.* **2017**, *586* (15), 650−657.

(18) Ray, H.; Perreault, F.; Boyer, T. Ammonia Recovery from Hydrolyzed Human Urine by Forward Osmosis with Acidified Draw Solution. *Environ. Sci. Technol.* **2020**, *54* (18), 11556−11565.

(19) Clark, B.; Tarpeh, W. Selective Recovery of Ammonia Nitrogen from Wastewaters with Transition Metal-Loaded Polymeric Cation Exchange Adsorbents. *Chem. - Eur. J.* **2020**, *26*, 10099−100112.

(20) Ray, H.; Saetta, D.; Boyer, T. H. Characterization of urea hydrolysis in fresh human urine and inhibition by chemical addition. *Environmental Science: Water Research & Technology.* **2018**, *4*, 87−98.

(21) Shin, C.; Szczuka, A.; Jiang, R.; Mitch, W. A.; Criddle, C. S. Optimization of reverse osmosis operational conditions to maximize ammonia removal from the effluent of an anaerobic membrane bioreactor. *Environmental Science: Water Research & Technology.* **2021**, *7*, 739−747.

(22) Randall, D. G.; Krahenbühl, M.; Köpping, I.; Larsen, T. A.; Udert, K. M. A novel approach for stabilizing fresh urine by calcium hydroxide addition. *Water Res.* **2016**, *95* (15), 361−369.

(23) Hellström, D.; Johansson, E.; Grennberg, K. Storage of human urine: acidification as a method to inhibit decomposition of urea. *Ecological Engineering.* **1999**, *12* (3−4), 253−269.

(24) Ek, M.; Bergström, R.; Bjurhem, J. E.; Björlenius, B.; Hellström, D. Concentration of nutrients from urine and reject water from anaerobically digested sludge. *Water Sci. Technol.* **2006**, *54* (11−12), 437−444.

(25) Lind, B.; Ban, Z.; Bydén. Volume reduction and concentration of nutrients in human urine. *Ecological Engineering.* **2001**, *16* (4), 561−566.

(26) Gulyas, H.; Bruhn, P.; Furmanska, M.; Hartrampf, K.; Kot, K.; Luttenberg, B.; Mahmood, Z.; Stelmaszewska, K.; Otterpohl, R. Freeze concentration for enrichment of nutrients in yellow water from no-mix toilets. *Water Sci. Technol.* **2004**, *50* (6), 61−68.

(27) Sanchez, J.; Ruiz, Y.; Auleda, J. M.; Hernandez, E.; Raventos, M. Review. Freeze Concentration in the Fruit Juices Industry. *Food Sci. Technol. Int.* **2009**, *15*, 303−315.

(28) Auleda, J. M.; Raventós, M.; Hernández, E. Calculation method for designing a multi-plate freeze-concentrator for concentration of fruit juices. *J. Food Eng.* **2011**, *107* (1), 27−35.

(29) Pazmiño, N.; Raventos, M.; Hernández, E.; Gulfo, R.; Robles, C.; Moreno, F. L.; Ruiz, Y. Continuous system of freeze concentration of sucrose solutions: Process parameters and energy consumption. *Journal of Food Technology and Preservation.* **2016**, *1* (1), 1−5.

(30) Zambrano, A.; Ruiz, Y.; Hernández, E.; Raventós, M.; Moreno, F. L. Freeze desalination by the integration of falling film and block freeze-concentration techniques. *Desalination* **2018**, *436*, 56−62.

(31) Dadrasnia, A.; de Bona Muñoz, I.; Yáñez, E. H.; Lamkaddam, I. U.; Mora, M.; Ponsá, S.; Ahmed, M.; Argelaguet, L. L.; Williams, P. M.; Oatley-Radcliffe, D. L. Sustainable nutrient recovery from animal manure: A review of current best practice technology and the potential for freeze concentration. *J. Cleaner Prod.* **2021**, *315* (15), 128106.

(32) Randall, D. G.; Nathoo, J. A succinct review of the treatment of Reverse Osmosis brines using Freeze Crystallization. *Journal of Water Process Engineering.* **2015**, *8*, 186−194.

(33) Rane, M. V.; Padiya, Y. S. Heat pump operated freeze concentration system with tubular heat exchanger for seawater desalination. *Energy Sustainable Dev.* **2011**, *15* (2), 184−191.

(34) Rane, M. V.; Uphade, D. B. Heat Pump for Energy-Efficient Sugarcane Juice Freeze Pre-concentration. *Sugar Tech* **2018**, *20* (5), 591−598.

(35) Ganrot, Z.; Dave, G.; Nilsson, E. Recovery of N and P from human urine by freezing, struvite precipitation and adsorption to zeolite and active carbon. *Bioresour. Technol.* **2007**, *98* (16), 3112−3121.

(36) Randall, D. G.; Nathoo, J. Resource recovery by freezing: A thermodynamic comparison between a reverse osmosis brine, seawater and stored urine. *Journal of Water Process Engineering.* **2018**, *26*, 242−249.

(37) Pradhan, S. K.; Holopainen, J. K.; Heinonen-Tanski, H. Stored Human Urine Supplemented with Wood Ash as Fertilizer in Tomato

https://doi.org/10.1021/acsestengg.1c00271
ACS EST Engg. XXXX, XXX, XXX−XXX

(Solanum lycopersicum) Cultivation and Its Impacts on Fruit Yield and Quality. *J. Agric. Food Chem.* **2009**, *57*, 7612−7617.
(38) American Public Health Association, American Water Works Association, Water Environment Federation. *Standard Methods for the Examination of Water and Wastewater*, 23rd ed; Washington, DC.
(39) United States Environmental Protection Agency. *Onsite Wastewater Treatment Systems Manual*. **2002**, Washington, DC.
(40) Schroeder, D. V. *An Introduction to Thermal Physics*; Addison Wesley Longman, 2000.
(41) Kumano, H.; Asaoka, T.; Saito, A.; Okawa, S. Study on latent heat of fusion of ice in aqueous solutions. *Int. J. Refrig.* **2007**, *30* (2), 267−273.
(42) Rauch-Williams, T.; Marshall, M. R.; Davis, D. J. Preparation of Baseline Data to Establish the Current Amount of Resource Recovery. *Water Environment Federation Report No. WSEC-2018-TR-003*, September **2018**. https://www.wef.org/globalassets/assets-wef/direct-download-library/public/03—resources/WSEC-2018-TR-003 (accessed July 19, 2021).

https://doi.org/10.1021/acsestengg.1c00271
ACS EST Engg. XXXX, XXX, XXX−XXX