

PAPER



Cite this: *Environ. Sci.: Water Res. Technol.*, 2021, 7, 2075

Emerging investigator series: thermodynamic and energy analysis of nitrogen and phosphorous recovery from wastewaters†

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In a circular nutrient economy, nitrogen and phosphorous are removed from waste streams and captured as valuable fertilizer products, to more sustainably reuse the resources in closed-loops and simultaneously protect receiving aquatic environments from harmful N and P emissions. For nutrient reclamation to be competitive with the existing practices of N fixation and P mining, the methods of recovery must achieve at least comparable energy consumption. This study employed the Gibbs free energy of separation to quantify the minimum energy required to recover various N and P fertilizer products from waste streams of fresh and hydrolyzed urine, greywater, domestic wastewater, and secondary treated wastewater effluent. The comparative advantages in theoretical energy intensities for N and P recovery from nutrient-dense waste streams, such as fresh and hydrolyzed urine, were assessed against the other more dilute sources. For example, compared to reclaiming the nutrients from treated wastewater effluent at centralized wastewater treatment plants, the minimum energy required to recover 1.0 M $\text{NH}_3(\text{aq})$ from source-separated hydrolyzed urine can be $\approx 40\text{--}68\%$ lower, whereas recovering $\text{KH}_2\text{PO}_4(\text{s})$ from diverted fresh urine can, in principle, be $\approx 13\text{--}34\%$ less energy intensive. The study also evaluated the efficiencies required by separation techniques for the energy demand of N and P recovery to be lower than the current production approaches of the Haber–Bosch process and phosphate rock mining. For instance, the most energetically favorable ammoniacal nitrogen and orthophosphate reclamation schemes, which target hydrolyzed and fresh urine, respectively, require energy efficiencies $>7\%$ and $>39\%$. This study highlights that strategic selection of waste stream and fertilizer product can enable the most expedient recovery of nutrients and realize a circular economy model for N and P management.

Received 5th August 2021,
Accepted 15th September 2021

DOI: 10.1039/d1ew00554e

rsc.li/es-water

Water impact

To attain a more sustainable circular economy model of nutrient management, N and P present in waste streams need to be recovered for reuse. This study quantitatively shows that recovery from nutrient-rich urine can be realized using separation techniques with technologically-achievable energy efficiencies. The sizable global energy savings provide impetus for broad implementation of nutrient recovery from discarded waste streams.

Introduction

Nitrogen and phosphorus are essential macronutrients for global food security and principal components of fertilizers. The prevailing Haber–Bosch process to fix atmospheric N_2 into bioavailable ammonia, NH_3 , is very energy-intensive ($8.9\text{--}19.3 \text{ kW h kg-N}^{-1}$) and accounts for 1–2% of the world's

annual energy consumption.^{1–3} Likewise, mining of phosphate rock, the dominant method of P production, requires large amounts of energy ($0.80\text{--}1.66 \text{ kW h kg-P}^{-1}$).^{4,5} Furthermore, phosphate deposits are a finite resource, with reserves predicted to last only 50–100 years and production projected to decline after 2033.^{6,7} On top of the substantial costs of industrial fertilizer production, energy and chemicals are additionally needed to manage the nutrients downstream, after consumption: nitrogen and phosphorus are pollutants and need to be separated from anthropogenic streams in wastewater treatment plants (WWTPs) before discharge to the environment.^{8–12} However, most WWTPs in the U.S. are not equipped with advanced tertiary treatments dedicated to nutrient elimination.¹³ When N and P are not adequately removed, the nutrients are discharged into aquatic

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1ew00554e

ecosystems and can cause eutrophication, harmful algal blooms, and hypoxic dead zones, which devastate the environment and reduce biodiversity.^{14–17} These ecotoxic environments can consequently pose public health threats as conventional drinking water treatment is ineffective in removing algal and cyanobacterial toxins.^{18,19} The biogeochemical flows of both N and P are, hence, flagged as violating the safe operating space for humanity and pose high risks under the planetary boundaries framework.²⁰

The significant adulteration of natural ecosystems by nutrient emissions patently highlights the critical shortcomings of the current approach for N and P management and starkly underscores the critical need for more sustainable nutrient management.^{21–23} The urgency of the problem was endorsed by the National Academy of Engineers, which identified an improved system for nitrogen management as a grand challenge for the 21st century.²⁴ There have been considerable efforts to reduce nutrient emissions from WWTPs,^{25–32} but the majority of the methods remove nutrients from wastewater (WW) without capture. This approach still contributes to the inefficiencies of the linear nutrient economy model, where nutrients are produced/extracted at immense costs and excess nutrients in wastewater are treated at an additional expense to avoid environmental and public health concerns. The challenges facing current nutrient management practices offer opportunities for synergistic solutions. A circular economy model advocates for the simultaneous removal and recovery of nutrients from waste-sources.^{33–36} N and P captured from wastewater can be recycled back into the food chain to close the nutrient loop, easing the demand for nitrogen fixation and phosphorus mining, and simultaneously alleviating potential harms to the environment and public health. The recovery of nutrients from waste streams for reuse is, therefore, a paradigm shift to a more sustainable approach for nutrient management.

The recovery of nutrients from various waste streams of the cycle, including urine,^{9,13,37–48} greywater,⁴⁹ domestic wastewater,^{50–54} and WWTP effluent,^{55–59} has been investigated in previous studies. A simplified schematic of the wastewater cycle and the principal streams is depicted in Fig. 1A. Note that the main form of nitrogen in fresh urine is urea, $\text{CO}(\text{NH}_2)_2$, which undergoes hydrolysis by naturally present urease enzymes to form ammoniacal nitrogen and bicarbonate, yielding hydrolyzed urine after $\approx 2\text{--}7$ d.^{60,61} As the waste streams undergo biological, chemical, and physical transformations along the cycle and combine with other flows, the compositions and aqueous chemistries are significantly altered.^{60,62–68} Similarly, the nutrient content can vary drastically. Fig. 1B shows the concentration range of total ammoniacal nitrogen, TAN, and total orthophosphate, TOP, (shaded green and patterned red bars, respectively) for the different waste streams. The TAN and TOP concentrations span over five orders of magnitude, with the general trend, in increasing order of nutrient content, being greywater < secondary (2°) WW effluent < domestic WW < fresh and hydrolyzed urine. Therefore, the various recovery

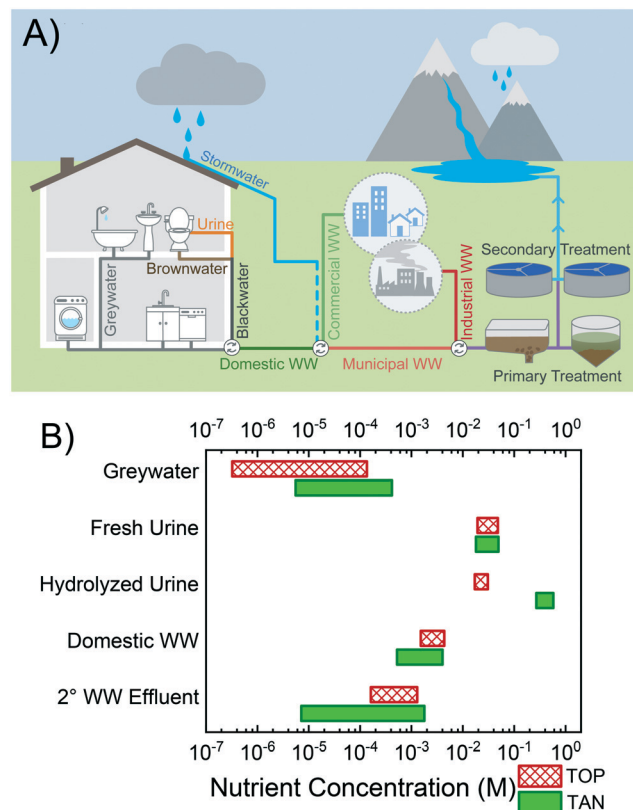


Fig. 1 A) Illustrative representation of wastewater sources and streams. The constituents of domestic wastewater (WW) are blackwater, the mixture of brownwater and urine, and greywater. Domestic WW combines with waste streams from commercial and industrial sources, and may be diluted by stormwater runoff in combined sewer systems before treatment at centralized facilities. Treated effluent is eventually discharged to the environment. B) Concentration range of total ammoniacal nitrogen, TAN, and total orthophosphate, TOP, (shaded green and patterned red bars, respectively) for waste streams of greywater, fresh urine, hydrolyzed urine, domestic WW, and secondary (2°) WW effluent.^{60,62–68}

technologies are targeting sources with widely disparate nutrient contents and with N and P in different chemical forms (e.g., nitrogenous compounds include ammonia, nitrate, nitrite, and urea).

Waste streams that are richer in nutrients should, intuitively, favor recovery efficiency and effectiveness. The advantages of high nutrient content for recovery have been qualitatively discussed in literature,^{13,39,69} but there are currently no rigorous quantitative analyses to more precisely value the benefits. In contrast, energy analyses had been conducted for other environmentally-relevant separations, such as reverse osmosis desalination, conventional thermal distillation, and membrane distillation,^{70–73} to reveal intrinsic limitations and thermodynamic insights of the processes. Applying similar analytical approaches to nutrient recovery can enhance fundamental understanding and shed light on the thermodynamic principles governing the separations, which can in turn inform efforts to capture N and P from the waste streams.

In this study, we conduct a thermodynamic analysis of nutrient recovery from different waste streams. First, governing equations for the theoretical minimum energy required to recover nutrients, determined using the Gibbs free energy of separation, are presented. The minimum energy to recover ammonia and phosphate is quantitatively assessed for different waste streams spanning a range of nutrient content, namely source-separated urine (fresh and hydrolyzed), greywater, domestic WW, and 2° WW effluent. Energy requirements to reclaim products of different nutrient species and concentrations are then examined. The impact of recovery yield on energy demand is evaluated and practical considerations are discussed. The energy to separate and capture other forms of N, specifically, nitrate and urea, is also explored. Next, we analyze the practical efficiency needed from actual processes for nutrient recovery from wastewaters to be competitive with conventional methods of N and P production, *i.e.*, NH₃ fixation by Haber–Bosch and phosphate mining. Finally, the implications of ammonia and phosphate separation from wastewaters are discussed and the benefits of nutrient recovery are highlighted.

Minimum energy of nutrient recovery

Gibbs free energy of separation is the minimum energy required to recover nutrients

In the recovery of nutrients from waste streams, the desired nutrient components of N and P are separated from the dilute feed to yield a nutrient-rich product, leaving a wastewater retentate stream less concentrated in N or P. The theoretical minimum energy required to achieve this nutrient recovery, E_{\min} , is equal to the Gibbs free energy of separation, ΔG_{sep} , which is the difference between the Gibbs free energy of the product and retentate (resultant streams), and the wastewater (initial feed), as described by eqn (1):

$$E_{\min} = \Delta G_{\text{sep}} = N_{\text{P}}G_{\text{P}} + N_{\text{R}}G_{\text{R}} - N_{\text{F}}G_{\text{F}} \quad (1)$$

where G is the molar Gibbs free energy, N is the total number of moles in each stream, and subscripts P, R, and F denote the product, retentate, and feed streams, respectively.

The molar Gibbs free energy of a mixed solution is the sum of the partial molar Gibbs free energy of the constituent species:^{74,75}

$$G = \sum x_i G_i^0 + RT \left[\sum x_i \ln(\gamma_i x_i) \right] \quad (2)$$

where x and γ are the mole fraction and activity coefficient of species i , G^0 is the Gibbs free energy of formation in the aqueous solution at standard state, R is the gas constant, and T is the absolute temperature.

By applying eqn (1) and (2), the Gibbs free energy of separation per mole of nutrient recovered, $\Delta \bar{G}_{\text{sep}}$, can be expressed as:

$$\Delta \bar{G}_{\text{sep}} = \frac{1}{x_{1,\text{P}}} \left\{ \begin{aligned} & \sum x_{i,\text{P}} G_{i,\text{P}} + RT \sum x_{i,\text{P}} \ln(\gamma_{i,\text{P}} x_{i,\text{P}}) \\ & + \frac{N_{\text{R}}}{N_{\text{P}}} \left[\sum x_{i,\text{R}} G_{i,\text{R}} + RT \sum x_{i,\text{R}} \ln(\gamma_{i,\text{R}} x_{i,\text{R}}) \right] \\ & - \frac{N_{\text{F}}}{N_{\text{P}}} \left[\sum x_{i,\text{F}} G_{i,\text{F}} + RT \sum x_{i,\text{F}} \ln(\gamma_{i,\text{F}} x_{i,\text{F}}) \right] \end{aligned} \right\} = \bar{E}_{\min} \quad (3)$$

where subscript 1 denotes the targeted nutrient component, *i.e.*, N or P species. Therefore, with the composition and relative proportion of the feed, product, and retentate streams, the theoretical minimum energy required to reclaim a mole of nutrient, \bar{E}_{\min} , can be determined using eqn (3). Note that for pure products, *i.e.*, solid minerals or unmixed liquids, the product $\sum x \ln \gamma x$ term vanishes and $x_{1,\text{P}}$ can be replaced with $n_{1,\text{P}}$, the number of N or P atoms in the chemical structure of the pure liquid/solid mineral product ($n_{1,\text{P}} = 1$ for all products except for (NH₄)₂SO₄, where $n_{1,\text{P}} = 2$). Recovery yield, Y , is defined as the fraction of nutrient available in the initial feed captured in the product stream, and can be described by:

$$Y_{i,\text{P}} = \frac{x_{1,\text{P}} N_{\text{P}}}{x_{1,\text{F}} N_{\text{F}}} \quad (4)$$

Note that, again, for solids and pure liquid products, $x_{1,\text{P}}$ is replaced with $n_{1,\text{P}}$.

Analysis of minimum energy for nutrient recovery

Detailed methodology to determine the molar minimum energy of nutrient recovery, \bar{E}_{\min} , is discussed in the ESI† and briefly presented here. Typical ranges of nutrient species mole fraction concentrations and pH values of the greywater, domestic WW, 2° WW effluent, fresh urine, and hydrolyzed urine feed waste streams are based on literature data (Table S1 in the ESI†),^{60,62–67} whereas $x_{1,\text{P}}$ and $n_{1,\text{P}}$ are dependent on the concentration and chemical structure of the product, respectively. Typical concentration ranges of other species in the waste streams of the analysis are presented in Table S2 in the ESI.^{†60,62–68} For a certain Y (and corresponding $x_{1,\text{P}}$ or $n_{1,\text{P}}$), the retentate composition is determined by mole balance and accounting for speciation due to pH and concentration changes. *I.e.*, the approach incorporates the effects of protonation/deprotonation on x of orthophosphates and ammoniacal nitrogen (H₃PO₄/H₂PO₄[−]/HPO₄^{2−}/PO₄^{3−} and NH₄⁺/NH₃, respectively). To understand the influence of recovery yield on \bar{E}_{\min} , Y of 0.005, 0.2, 0.5, 0.8, and 1.0 are modeled for select wastewater matrices of 2° WW effluent and hydrolyzed urine. Because the complete water chemistry of most wastewater feeds is not fully known (*i.e.*, species composition and buffering capacity), the analysis is able to only consider the capture of an infinitesimally small amount of nutrient, *i.e.*, $Y \rightarrow 0$, such that the feed and retentate compositions are effectively identical. The complete equations utilized to determine the molar Gibbs free energy

of separation for all scenarios in the analysis are presented in the ESI,† eqn (S5)–(S20).

All calculations model recovery at $T = 298$ K. Non-ideal behavior in solutions was accounted for using activity coefficients, γ_i , which were determined using the Davies approximation,³⁷ nonrandom two-liquid method,^{76,77} or experimental data reported in the literature,⁷⁸ as described in the ESI.† The G^0 for each species i in aqueous solution can be found in Table S3 in the ESI.† For pure liquids and solid minerals, the Gibbs free energy of the product is equal to the Gibbs free energy of formation at standard state, $G_P = G_{f,P}^0$ (values are presented in Table S4 of the ESI.†).

Energy requirement for nutrient recovery

Harvesting ammonia from more concentrated waste streams requires less energy

The molar minimum energy (*i.e.*, per mole of NH_3 captured) required to recover liquid ammonia, $\text{NH}_3(\text{l})$, from different waste streams of varying TAN concentrations is calculated using eqn (S5) of the ESI† and presented in Fig. 2. Yields of 1 and 0, representing complete recovery of N in the product and capture of an infinitesimally small amount of N from the feed, respectively, were analyzed (solid and dashed lines). Typical TAN concentration ranges in the various waste streams are shown as floating bars and correspond to the horizontal axis (logarithmic scale). To isolate the impact of $[\text{TAN}]$ on \bar{E}_{min} , the analysis for $Y = 1$ assumes the feed waste streams to have $\text{pH} \ll \text{p}K_a$ of NH_4^+ (9.24) and inexhaustible

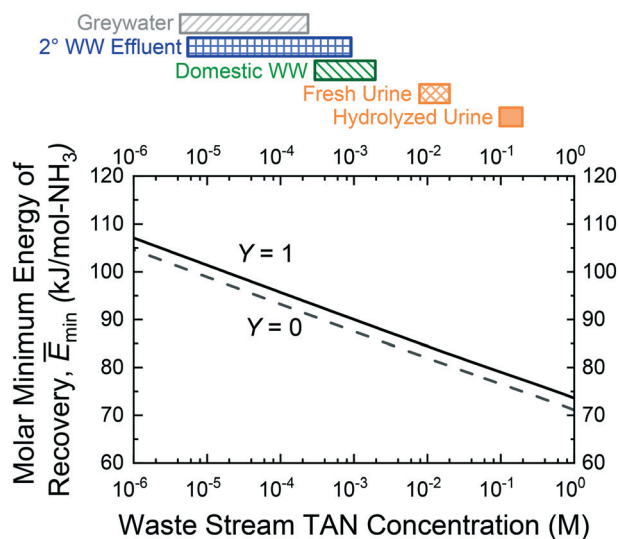


Fig. 2 Molar minimum energy, \bar{E}_{min} , required to recover the nutrient product of pure liquid ammonia as a function of waste stream TAN concentration for recovery yields, Y , of 1 and 0 (solid and dashed lines, respectively). Floating bars, corresponding to the horizontal axis (on logarithmic scale), represent the TAN concentration ranges for waste streams of greywater, secondary wastewater effluent, domestic wastewater, fresh urine, and hydrolyzed urine. For simplification of analysis, all TAN in the waste streams was assumed to be present as NH_4^+ .

buffering capacity, such that the predominant form of TAN in both the feed and retentate is NH_4^+ ; the influence of $\text{NH}_4^+/\text{NH}_3(\text{aq})$ speciation is considered in the next subsection. We note that the pH values of all waste streams examined in this study, except for hydrolyzed urine, are usually well below 9.24 and, hence, TAN is mostly present as ammonium.^{60,62–68}

As expected, Fig. 2 demonstrates that to minimize the theoretical minimum energy required to capture $\text{NH}_3(\text{l})$, it is advantageous to target waste streams with high TAN concentrations. This trend is consistent with thermodynamic assessments of desalination, where \bar{E}_{min} for water recovery increases with feed salinity.^{70,71} The minimum energy required to reclaim $\text{NH}_3(\text{l})$ essentially decreases linearly with increasing logarithm of TAN concentration in the waste stream, *i.e.*, $\bar{E}_{\text{min}} \approx \propto -\log[\text{TAN}]$, primarily due to the $\ln x$ terms of eqn (3). The slight deviation from perfect linearity is attributed to the non-linear dependence of $\gamma_{\text{NH}_4^+}$ on ionic strength (Davies approximation, eqn (S21) in the ESI.†).³⁷ In other words, the reduction in \bar{E}_{min} is not proportional to the increase in $[\text{TAN}]$ of the feed stream. Concentrated streams, such as hydrolyzed and fresh urine, have orders of magnitude more TAN than diluted streams of domestic wastewater, secondary wastewater effluent, and greywater; however, the \bar{E}_{min} is not orders of magnitude higher when capturing N from the diluted streams compared to the more concentrated streams. For example, hydrolyzed urine is $\approx 140\text{--}520\times$ more concentrated in TAN than domestic wastewater, but the \bar{E}_{min} for the product of $\text{NH}_3(\text{l})$ at $Y = 0$ is only 1.13–1.22 \times greater for domestic WW.

Recovery yields of 1 and 0 exhibit similar trends, with \bar{E}_{min} for $Y = 1$ approximately 3% higher than $Y = 0$ across the TAN concentrations investigated. As Y increases, NH_3 is separated from a progressively more dilute feed stream, thus requiring more energy and the averaged molar energy of separation rises. Again, parallels can be drawn to the increasing specific energy of desalination for larger water recovery yields.^{15,16} However, the magnitude of \bar{E}_{min} increase for higher nutrient recoveries is drastically smaller than that for desalination, where the energy requirement almost doubles when Y is raised from 0 to 0.5. Because the \bar{E}_{min} between complete recovery and capturing an infinitesimally minute amount (*i.e.*, $Y = 1$ and 0, respectively) differs only by $\approx 3\%$, examination of \bar{E}_{min} for $Y = 0$ is informative of practical, nonzero recovery yields. Most of the subsequent analyses in this study evaluate \bar{E}_{min} at $Y = 0$, while the impact of recovery yield on \bar{E}_{min} will be discussed in depth in a latter section.

Feed stream pH affects \bar{E}_{min} by influencing speciation

\bar{E}_{min} values to recover select ammonia and phosphate products from various waste streams are shown in Fig. 3A and B, respectively. The N products of liquid ammonia, $\text{NH}_3(\text{l})$, aqueous ammonia solutions at 10, 5.0, and 1.0 M, and solid precipitate of ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4(\text{s})$, are common commercial fertilizers.^{79–82} Likewise, solid precipitate P products of potassium

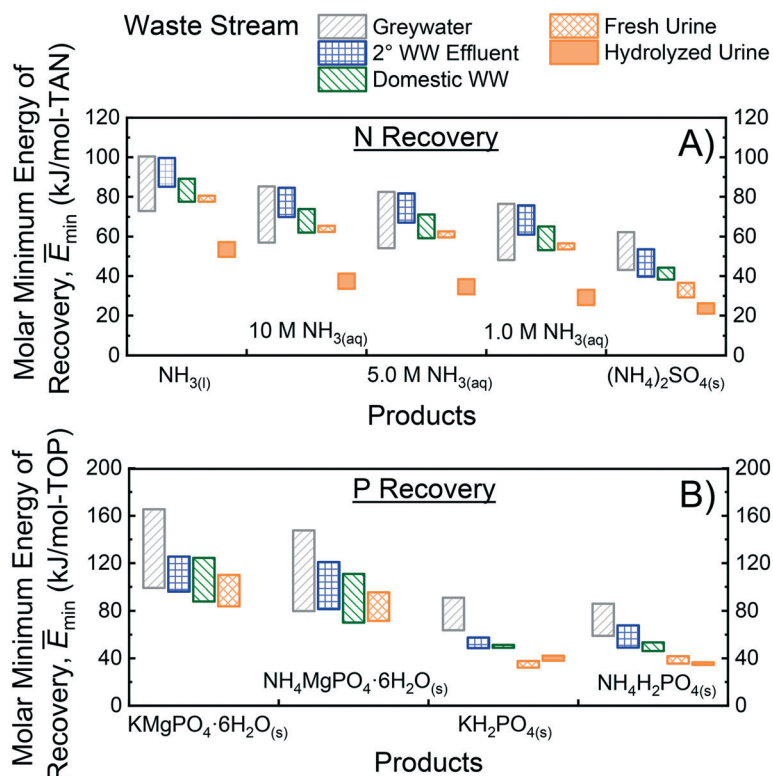


Fig. 3 Molar minimum energy, \bar{E}_{\min} , required to recover A) TAN as products of liquid ammonia, $\text{NH}_3(\text{l})$, 10, 5.0, and 1.0 M aqueous ammonia solutions, and ammonium sulfate solid, $(\text{NH}_4)_2\text{SO}_4(\text{s})$; and B) TOP as mineral products of potassium magnesium phosphate, $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$, struvite, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$, potassium phosphate, KH_2PO_4 , and monoammonium phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$. Waste stream sources are greywater, secondary wastewater effluent, domestic wastewater, fresh urine, and hydrolyzed urine. Floating columns indicate the \bar{E}_{\min} ranges that correspond to the typical span of nutrient content, product co-species concentrations, and pH reported for the waste streams. The analysis considered recovery yield of 0 for all products, *i.e.*, an infinitesimally minute amount of nutrient is recovered from the waste stream.

magnesium phosphate, $\text{KMgPO}_4 \cdot 6(\text{H}_2\text{O})$, struvite, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$, potassium phosphate, KH_2PO_4 , and monoammonium phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$, are also conventional fertilizers available in the market.^{82–89} Because each waste stream can be highly heterogeneous in nutrient content, concentrations of product co-species (*e.g.*, SO_4^{2-} is co-species for the $(\text{NH}_4)_2\text{SO}_4(\text{s})$ product), and pH, the resultant energy requirement spans a range of values (according to eqn (3)). The top and bottom of the floating bars represent the highest and lowest \bar{E}_{\min} , respectively, for each waste stream and product pair. Detailed \bar{E}_{\min} values for all conditions, calculated using eqn (S5)–(S12),[†] can be found in Tables S5 and S6 of the ESI.[†]

As previously discussed, the TAN concentration in the waste stream is a primary factor influencing \bar{E}_{\min} : the minimum energy required to capture ammonia products is generally lower when targeting waste streams of higher [TAN], such as hydrolyzed urine, compared to more diluted streams. Additionally, \bar{E}_{\min} is also dependent on the pH of the waste stream. For a certain waste stream [TAN], \bar{E}_{\min} values for the selected products are lower in N recovery scenarios with higher waste stream pH (Table S5[†]). As an illustration, Fig. 4 presents \bar{E}_{\min} for products recovered from greywater with [TAN] = 2.11×10^{-4} M (midpoint of concentration range), but at different pH values.

The \bar{E}_{\min} required to recover 1.0 M $\text{NH}_3(\text{aq})$ from greywater at pH of 9.0 is 25.1% less than that at pH of 5.0. Because

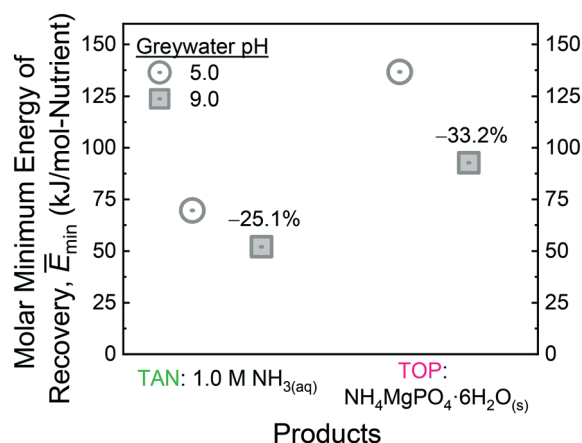


Fig. 4 Molar minimum energy, \bar{E}_{\min} , required to recover the TAN product of 1.0 M $\text{NH}_3(\text{aq})$ and the TOP product of struvite, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$, from greywater at pH of 5.0 and 9.0 (open circle and filled square symbols, respectively). Labels above the symbols indicate the percent decrease in \bar{E}_{\min} from feed pH of 5.0 to 9.0. Mid-range greywater TAN and TOP concentrations of 2.11×10^{-4} M and 6.80×10^{-5} M, respectively, are utilized in this analysis and the recovery yield of the product is 0 (*i.e.*, an infinitesimally small quantity of nutrient is recovered from the waste stream).

ammonia is a weak base, which can protonate to form ammonium, the fraction of TAN present as $\text{NH}_{3(\text{aq})}$ rises with increasing pH (eqn (S1) in the ESI†). The standard-state molar Gibbs free energy of formation of $\text{NH}_{3(\text{aq})}$ is higher than that of NH_4^+ ($-26.6 \text{ kJ mol}^{-1}$ compared to $-79.3 \text{ kJ mol}^{-1}$, Table S3†) and, thus, the Gibbs free energy of separation is lower for $\text{NH}_{3(\text{aq})}$ than NH_4^+ , as per eqn (3). Hence, the recovery of the N products is thermodynamically more favorable if TAN is present as $\text{NH}_{3(\text{aq})}$ in more basic waste streams. The theoretical minimum energy required to reclaim N from hydrolyzed urine is significantly lower than those of other waste streams (Fig. 3A) because of the two advantages of higher pH and greater TAN concentration. The hydrolyzed urine pH range is 9–9.2, close to or at the pK_a of 9.24 for ammonium, whereas the pH of the other waste streams is mostly ≈ 5 –8.5. Also, [TAN] is 0.270–0.578 M for hydrolyzed urine, at least 67× greater than other N sources aside from fresh urine (still 5.5–32.2× higher). However, the energy benefits for $(\text{NH}_4)_2\text{SO}_{4(\text{s})}$ recovery from hydrolyzed urine are less pronounced (Fig. 3A), because N is captured as NH_4^+ . Converting $\text{NH}_{3(\text{aq})}$, the predominant TAN species in hydrolyzed urine, to ammonium increases ΔG_{sep} and offsets the beneficial G^0 effect. Overall, waste streams with both high TAN concentration and pH offer the smallest \bar{E}_{min} to overcome for N recovery; of the waste streams examined here, hydrolyzed urine is the most optimal.

Among the N products evaluated, \bar{E}_{min} is generally highest for $\text{NH}_{3(\text{l})}$, followed by 10 M $\text{NH}_{3(\text{aq})}$, 5.0 M $\text{NH}_{3(\text{aq})}$, 1.0 M $\text{NH}_{3(\text{aq})}$, and then $(\text{NH}_4)_2\text{SO}_{4(\text{s})}$ (Fig. 3A). For the aqueous ammonia solutions, \bar{E}_{min} decreases with lower product concentration. This is reflected in eqn (S7)† and also intuitively understood: a more dilute product stream requires less separation from the feed and, hence, demands less energy. For the pure products of $\text{NH}_{3(\text{l})}$ and $(\text{NH}_4)_2\text{SO}_{4(\text{s})}$, \bar{E}_{min} is largely dependent on the Gibbs free energy of formation of the product, $G_{\text{f,P}}^0$ (Table S4 in the ESI†), with a lower $G_{\text{f,P}}^0$ contributing to a smaller \bar{E}_{min} . Because $G_{\text{f},(\text{NH}_4)_2\text{SO}_{4(\text{s})}}^0 \ll G_{\text{f},\text{NH}_{3(\text{l})}}^0$, recovering $(\text{NH}_4)_2\text{SO}_{4(\text{s})}$ is thermodynamically more favorable than $\text{NH}_{3(\text{l})}$.

Rational selection of waste stream feed and products minimizes energy for nutrient recovery

Similar trends are also observed for TOP recovery (Fig. 3B and 4). Note that because magnesium precipitates out from urine during hydrolysis,^{60,61,90} $[\text{Mg}^{2+}]$ in hydrolyzed urine is practically negligible and, hence, recovery of Mg-based P products, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}_{(\text{s})}$, and $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}_{(\text{s})}$, was not analyzed. Higher concentrations of TOP and product co-species (TAN, K^+ , and Mg^{2+}) in the waste stream lowered \bar{E}_{min} . TOP concentrations in the waste streams follow the trend: greywater < secondary wastewater effluent < domestic wastewater < hydrolyzed urine < fresh urine, resulting in \bar{E}_{min} values largely following the reverse trend, *i.e.*, P recovery from fresh urine generally has the lowest \bar{E}_{min} . However, one deviation is the separation of $\text{NH}_4\text{H}_2\text{PO}_{4(\text{s})}$ from hydrolyzed

urine. This is due to the low concentration of the product co-species, NH_4^+ , significantly contributing to \bar{E}_{min} . Although fresh urine is richer in TOP (1.13–1.57×), [TAN] is only 0.067–0.085 that of hydrolyzed urine.

Despite fresh urine having significantly higher [TOP], the molar minimum energies of recovery for struvite, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}_{(\text{s})}$, and potassium magnesium phosphate (KMP), $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}_{(\text{s})}$, are comparable with the lower \bar{E}_{min} range for the more dilute streams of domestic WW, 2° WW effluent, and greywater. This is because P is present in struvite and KMP as PO_4^{3-} , the least protonated form of phosphate, and a greater portion of TOP in the feed exists as PO_4^{3-} at higher pH values. The pH range for fresh urine (6–7.5) is lower than domestic wastewater and secondary-treated wastewater effluent (6.5–8.5 and 6.8–7.7, respectively) and is considerably below the high-end of greywater (pH = 9). In the recovery of struvite and KMP from fresh urine, the deprotonation of H_2PO_4^- (predominant species below pH of 7.2) to PO_4^{3-} increases ΔG_{sep} , and partially nullifies the benefits of the high [TOP]. Therefore, \bar{E}_{min} is not substantially lower than other waste streams at higher pH (Table S6†). The impact of pH on \bar{E}_{min} is further illustrated by Fig. 4, which shows the \bar{E}_{min} of struvite recovery from greywater at pH = 5.0 and 9.0. The \bar{E}_{min} at pH = 9.0 is markedly depressed (–33.2%) relative to that at pH of 5.0. As the dominant forms of phosphate at pH = 5.0 and 9.0 are H_2PO_4^- and HPO_4^{2-} , respectively, less energy is required for the conversion to PO_4^{3-} with the more basic feed stream. This trend is observed for struvite and KMP across the different waste streams (Table S6†) and also corroborated by experimental observations that the two minerals precipitate more readily in higher pH solutions.⁹¹ In contrast, the effect of pH on \bar{E}_{min} is negligible for KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$, where P is present as H_2PO_4^- (Table S6†).

The most thermodynamically favorable products for P recovery are $\text{KH}_2\text{PO}_{4(\text{s})}$ and $\text{NH}_4\text{H}_2\text{PO}_{4(\text{s})}$, followed by $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}_{(\text{s})}$ and $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}_{(\text{s})}$, with \bar{E}_{min} primarily affected by the phosphate identity (H_2PO_4^- or PO_4^{3-}) and feed concentrations of product co-species (specifically Mg^{2+}). The acid dissociation constants of phosphoric acid are 2.2, 7.2, and 12.4. For the waste streams investigated here, the typical pH ranges between 5 and 9.2. Hence, the predominant phosphate species are H_2PO_4^- or HPO_4^{2-} . Because the conversion of the predominant phosphate species to H_2PO_4^- (no reaction or protonation of one H^+) needed to form $\text{KH}_2\text{PO}_{4(\text{s})}$ and $\text{NH}_4\text{H}_2\text{PO}_{4(\text{s})}$ requires less energy than the conversion to PO_4^{3-} (deprotonation of one or two H^+), \bar{E}_{min} is larger for struvite and KMP. Furthermore, the formation of struvite and KMP requires Mg^{2+} in addition to NH_4^+ and K^+ , respectively. The separation of Mg^{2+} from waste streams with low $[\text{Mg}^{2+}]$ adds to the energy cost, hence, contributing to the greater \bar{E}_{min} for $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}_{(\text{s})}$ and $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}_{(\text{s})}$.

For nutrient recovery from waste streams, it is advantageous to minimize energy requirements, thus a low \bar{E}_{min} is desirable. The main factors influencing the molar minimum energy for nutrient recovery are: nutrient concentrations in the feed, waste stream pH, and co-species

in the product. To minimize \bar{E}_{\min} , waste streams and products can be strategically targeted. Hydrolyzed urine and fresh urine, which contain the highest concentrations of TAN and TOP, respectively, are almost always the most optimal streams for TAN and TOP recovery. However, depending on the product, certain waste streams may be better suited because of the more favorable pH and co-species concentration. Therefore, the selection of product should be informed by the pH, availability of nutrients, and co-species in the specific waste stream.

Impact of nutrient recovery yields on minimum energy of recovery

Previous analysis modeled \bar{E}_{\min} for capturing various products from different waste streams at $Y = 0$. However, actual nutrient recovery will have nonzero recovery yields. Fig. 5 shows the \bar{E}_{\min} of select ammonia products of 1.0 M NH_3 aqueous solution and $\text{NH}_3(\text{l})$ (open and filled symbols, respectively) from two waste streams of secondary wastewater effluent and hydrolyzed urine (blue square and orange circle symbols, respectively) as a function of NH_3 recovery yield. As discussed previously, at $Y = 0$, *i.e.*, infinitesimally small NH_3 recovery, the pH and TAN speciation in the feed and retentate are essentially equal. However, at higher recovery yields, the pH and TAN speciation in the retentate stream differ significantly from the feed stream. Therefore, to calculate \bar{E}_{\min} for $Y > 0$, the speciation of TAN (*i.e.*, fraction of TAN as $\text{NH}_3(\text{aq})$ and NH_4^+ , denoted by α_{NH_3} and $\alpha_{\text{NH}_4^+}$, respectively) in both the feed and retentate stream must be considered in

conjunction with the TAN material balance (*i.e.*, $x_{\text{TAN},\text{F}}N_{\text{F}} + x_{\text{TAN},\text{RXN}}N_{\text{RXN}} = x_{\text{TAN},\text{P}}N_{\text{P}} + x_{\text{TAN},\text{R}}N_{\text{R}}$).

For scenarios with secondary wastewater effluent (blue square symbols), the feed stream $\text{pH} \ll \text{p}K_{\text{a}}$, which results in nearly complete predominance of NH_4^+ over $\text{NH}_3(\text{aq})$ (*i.e.*, $\alpha_{\text{NH}_4^+} \approx 1$ and $\alpha_{\text{NH}_3} \approx 0$). Because removing basic NH_3 leaves the remaining solution more acidic, the pH of the retentate stream is always lower than the feed stream pH. Therefore, TAN speciation values in the feed and retentate streams for 2° WW effluent are essentially equal, with $\alpha_{\text{NH}_4^+, \text{R}} \approx \alpha_{\text{NH}_4^+, \text{F}} \approx 1$ and $\alpha_{\text{NH}_3, \text{R}} \approx \alpha_{\text{NH}_3, \text{F}} \approx 0$. Increasing Y results in a slight increase in \bar{E}_{\min} for both $\text{NH}_3(\text{l})$ and 1.0 M $\text{NH}_3(\text{aq})$ recovery. This trend is consistent with Fig. 2, which also simulated waste streams with NH_4^+ as the predominant form of TAN. Importantly, \bar{E}_{\min} only marginally increases (<4%) between $Y = 0$ and 1. Thus, actual nutrient recovery applications can take advantage of this by striving for higher yields without significantly raising the theoretical energy requirement.

For hydrolyzed urine (orange circle symbols in Fig. 5), the feed pH is near the $\text{p}K_{\text{a}}$ of ammonium, such that $\alpha_{\text{NH}_3} \neq 0$. Thus at $Y > 0$, TAN speciation values in the feed and retentate streams differ significantly, *i.e.*, $\alpha_{\text{NH}_3, \text{R}} \neq \alpha_{\text{NH}_3, \text{F}}$ and $\alpha_{\text{NH}_4^+, \text{R}} \neq \alpha_{\text{NH}_4^+, \text{F}}$. An in-depth discussion of the methodology to account for this differing speciation can be found in the ESI.† In contrast to 2° WW effluent, the trends for \bar{E}_{\min} of $\text{NH}_3(\text{l})$ and 1.0 M $\text{NH}_3(\text{aq})$ recovery from hydrolyzed urine are not monotonic, but instead exhibit L-shaped rebounds with initial sharp decreases followed by gradual increases. This signifies that reclaiming the first molecule of NH_3 from hydrolyzed urine requires, in theory, more energy than the next molecules until a certain amount of ammonia is recovered and, thereafter, capturing every additional NH_3 molecule requires more energy than the last. In contrast to secondary wastewater effluent, the \bar{E}_{\min} of hydrolyzed urine changes significantly as a function of recovery yield. The distinction between the \bar{E}_{\min} trends of the two waste streams is due to the disparate speciation of TAN in the retentates. For 2° WW effluent scenarios, $\alpha_{\text{NH}_4^+, \text{R}}$ and $\alpha_{\text{NH}_3, \text{R}}$ are effectively independent of Y and, therefore, the concentrations of both NH_4^+ and $\text{NH}_3(\text{aq})$ in the retentate consistently decrease with higher yields. However, for hydrolyzed urine scenarios, the pH of the retentate significantly declines at higher yields and, thus, $\alpha_{\text{NH}_4^+, \text{R}}$ increases and $\alpha_{\text{NH}_3, \text{R}}$ decreases (see ESI† Tables S8 and S9 for pH and speciation in the feed and retentate at different Y , for products of $\text{NH}_3(\text{l})$ and 1.0 M $\text{NH}_3(\text{aq})$, respectively). Because the magnitude of the Gibbs free energy of formation for NH_4^+ is much greater than that for $\text{NH}_3(\text{aq})$ (-79.3 and -26.6 kJ mol^{-1} , respectively), NH_4^+ is the thermodynamically preferred form of TAN in solution. This results in competing factors affecting \bar{E}_{\min} : TAN in the retentate decreases with increasing yield, which drives \bar{E}_{\min} to increase, but this is countered by the reduction in \bar{E}_{\min} as the fraction of TAN present as NH_4^+ in the retentate increases with increasing yield. At low Y , the latter factor is more dominant, thus explaining the initial dip in \bar{E}_{\min} . With greater Y , retentate

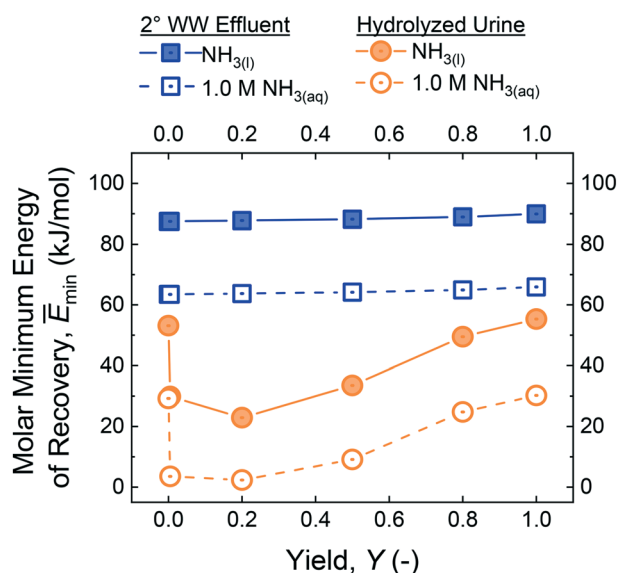


Fig. 5 Molar minimum energy, \bar{E}_{\min} , required to recover NH_3 as products of liquid ammonia, $\text{NH}_3(\text{l})$, or 1.0 M $\text{NH}_3(\text{aq})$ aqueous solution (filled and open symbols, respectively) from secondary wastewater effluent and hydrolyzed urine (blue square and orange circle symbols, respectively) as a function of recovery yield, Y (0, 0.005, 0.2, 0.5, 0.8, and 1). The mid-range TAN and pH of 2° WW effluent and hydrolyzed urine were utilized for this analysis.

pH drops and NH_4^+ becomes increasingly predominant over $\text{NH}_3(\text{aq})$. Beyond a certain point, the former factor dominates and \bar{E}_{min} increases. Further quantitative analysis and a more detailed discussion can be found in the ESI.†

Nitrate and urea are other forms of nitrogen suitable for recovery

In addition to ammoniacal products of $\text{NH}_3(\text{l})$, $\text{NH}_3(\text{aq})$, and $\text{NH}_4\text{SO}_4(\text{s})$, N can be recovered in other forms, such as nitrate, NO_3^- , and urea, $\text{CO}(\text{NH}_2)_2$.^{80,82} Nitrate is present in greywater, domestic wastewater, and secondary wastewater effluent (but is only present in negligible amounts in fresh or hydrolyzed urine), whereas urea is excreted in fresh urine (upon storage, the compound hydrolyzes into TAN and bicarbonate and, thus, urea is not present in significant quantities in the other waste streams). Fig. 6 shows the range of molar minimum energies required to reclaim aqueous and solid products containing NO_3^- from 2° WW effluent, as well as aqueous and solid urea from fresh urine. Based on compiled literature data, the nitrate concentration in secondary wastewater effluent spans from 0.0714–1.42 mM and the urea concentration range in fresh urine is 126–265 mM (252–530 mM-N).^{60,62–68} To calculate \bar{E}_{min} for 1.0 M $\text{KNO}_3(\text{aq})$, 1.0 M $\text{NH}_4\text{NO}_3(\text{aq})$, $\text{KNO}_3(\text{s})$, and $\text{NH}_4\text{NO}_3(\text{s})$ recovery from 2° WW effluent, eqn (S13)–(S16)† were used, respectively; to calculate the \bar{E}_{min} required to recover 1.0 M $\text{CO}(\text{NH}_2)_2(\text{aq})$ and $\text{CO}(\text{NH}_2)_2(\text{s})$ from fresh urine, eqn (S17) and (S18)† were utilized, respectively. Note that, for every mole of product, $\text{CO}(\text{NH}_2)_2$ and NH_4NO_3 contain 2 moles of N, whereas KNO_3 has only 1 mole of N.

The recovery of urea products from fresh urine is less energy demanding than the recovery of nitrate products from secondary wastewater effluent. This is attributed to urea being over 100-fold more concentrated in fresh urine than nitrate and the product co-species (NH_4^+ and K^+) are in 2° WW effluent. As discussed previously, \bar{E}_{min} is lower when capturing products from a more concentrated waste stream. For the

aqueous products, \bar{E}_{min} is lowest for $\text{CO}(\text{NH}_2)_2(\text{aq})$ followed by $\text{NH}_4\text{NO}_3(\text{aq})$, then $\text{KNO}_3(\text{aq})$. For solid products, $\text{NH}_4\text{NO}_3(\text{s})$ recovery from secondary wastewater effluent has the highest \bar{E}_{min} . This is because the Gibbs free energy required to form solid NH_4NO_3 from the initial species of aqueous NH_4^+ and NO_3^- in the feed is greater than that for $\text{CO}(\text{NH}_2)_2(\text{s})$ and $\text{KNO}_3(\text{s})$ (Table S10 in the ESI†). Generally, the recovery of 1.0 M aqueous products is thermodynamically more favorable than pure solids. This can be intuitively understood: producing solids requires the separation of all the water from the minerals, whereas less water needs to be removed to yield aqueous solutions. Furthermore, ordering free ions in aqueous solution into a solid crystal lattice incurs an additional entropic energy penalty, which further raises \bar{E}_{min} . However, there can be exceptions to the rule. Specific scenarios of pH-dependent speciation in the feed and Gibbs free energy of formation of the solid product can yield opposite trends. An example of such a deviation is the higher \bar{E}_{min} for the recovery of 1.0 M $\text{NH}_3(\text{aq})$ than for $\text{NH}_4\text{SO}_4(\text{s})$ (Fig. 3).

The \bar{E}_{min} values required to reclaim aqueous nitrate products, 1.0 M $\text{KNO}_3(\text{aq})$ and 1.0 M $\text{NH}_4\text{NO}_3(\text{aq})$, from 2° WW effluent are less than that for 1.0 M $\text{NH}_3(\text{aq})$ recovery from hydrolyzed urine, which is the lowest \bar{E}_{min} for aqueous TAN recovery in Fig. 3. The \bar{E}_{min} values required to recover solid nitrate products, $\text{KNO}_3(\text{s})$ and $\text{NH}_4\text{NO}_3(\text{s})$, from 2° WW effluent are also comparable to or lower than that for the recovery of TAN product ($\text{NH}_4)_2\text{SO}_4(\text{s})$ from all waste streams other than fresh and hydrolyzed urine. These comparisons suggest that, in principle, recovering nitrate from 2° WW effluent may be an equally or more favorable alternative to TAN recovery. However, the Gibbs free energy to reduce nitrate to the bio-preferred form of N—ammonia, NH_3 —is 591 kJ mol^{-1} .³ The additional energy requirement to reduce the oxidation state of N from +5 to -3 (8 electrons) is an order of magnitude higher than the \bar{E}_{min} for TAN recovery. The better suitability of NH_3 as a fertilizer and the huge energy cost needed to convert nitrate to ammonia, thus, indicate that targeting TAN over NO_3^- would be more prudent for nutrient recovery. \bar{E}_{min}

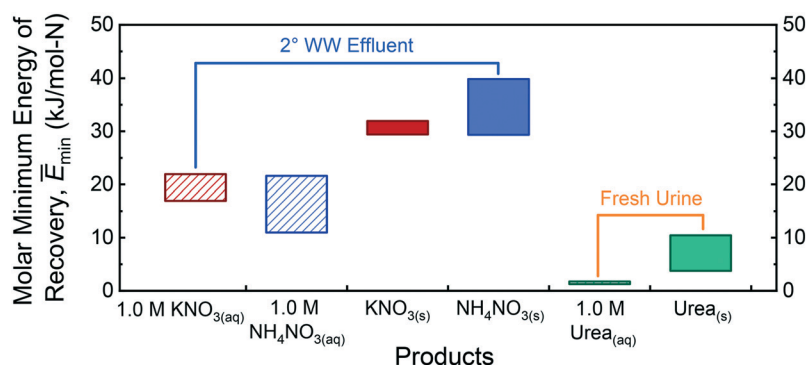


Fig. 6 Molar minimum energy, \bar{E}_{min} , required to recover different N products from waste streams of secondary wastewater effluent and fresh urine. Products recovered from 2° WW effluent are 1.0 M $\text{KNO}_3(\text{aq})$, 1.0 M $\text{NH}_4\text{NO}_3(\text{aq})$, $\text{KNO}_3(\text{s})$, and $\text{NH}_4\text{NO}_3(\text{s})$, whereas products reclaimed from fresh urine are 1.0 M aqueous urea solution, $\text{CO}(\text{NH}_2)_2(\text{aq})$, and solid urea, $\text{CO}(\text{NH}_2)_2(\text{s})$. Patterned and shaded columns denote aqueous and solid products, respectively. Floating columns indicate the \bar{E}_{min} ranges that correspond to the typical span of nutrient content, product co-species concentrations, and pH reported for the waste streams. The recovery yield is 0 for all products, i.e., an infinitesimally minute amount of nutrient is recovered from the waste stream.

values required to capture urea as aqueous and solid products from fresh urine are significantly lower than the different TAN product and waste stream pairing examined here. Specific pros and cons of different nitrogen fertilizers aside,^{92–94} the theoretically less energy-intensive path provides impetus to pursue the realization of urea recovery from fresh urine.

Presence of other species in wastewater matrix marginally increases energy demand for nutrient recovery

Analyses presented earlier consider the feed streams as simplified solutions containing only species required for the product (*i.e.*, nutrients and co-species), in addition to H₂O, OH[−], and H⁺. However, actual waste streams are complex water matrices with many other solutes, including different ions and neutral compounds. Na⁺ and Cl[−] are two prominent ionic species universally present in all the examined waste streams (*e.g.*, NaCl concentrations in secondary wastewater effluent and hydrolyzed urine are 1.41–17.4 and 64.9–119 mM, respectively). To quantify the influence of species passive to the nutrient recoveries, such as NaCl, \bar{E}_{\min} values are evaluated for the capture of NaCl-free NH_{3(l)} and 1.0 M NH_{3(aq)} from secondary wastewater effluent and hydrolyzed urine using eqn (S6) and (S7)[†] (with 0 mM NaCl) and eqn (S19) and (S20)[†] (with 9.40 and 88.9 mM NaCl in the feeds, respectively). Because the recovered products do not contain the passive species NaCl, the difference in \bar{E}_{\min} signifies the additional energy required to separate the nutrients from Na⁺ and Cl[−] present in the waste streams. In this analysis, mid-range TAN content, NaCl concentration, and pH of the waste streams were utilized. Detailed results are presented in Table S11 in the ESI.[†]

The inclusion of passive species in the determination of \bar{E}_{\min} results in only miniscule added energy requirements of 0.10–1.89% across the investigated scenarios. When NaCl in the waste stream is considered, \bar{E}_{\min} is marginally higher due to the additional energy required to separate TAN from Na⁺ and Cl[−], in addition to H₂O. However, because NaCl is present at substantially lower concentrations compared to H₂O at ≈ 55 mol L^{−1} (*i.e.*, the waste streams are >99% water, even for the most saline feeds), this increase is minimal. Therefore, the ubiquitous presence of passive species in the waste streams has a negligible impact on the theoretical energy required to recover N and P nutrients. Nonetheless, the purity of the product and the presence of undesired species, such as Na⁺, are important metrics for the resultant fertilizers.

Energy intensity of N and P recovery from waste streams can be competitive with conventional nutrient production

The energy demand discussed so far is the theoretical minimum, but in practical nutrient recovery processes, the actual energy required to capture N and P will be higher than \bar{E}_{\min} due to inevitable inefficiencies of the recovery techniques. This analysis examines the practical molar energy of recovery, \bar{E}_{prac} , defined as the energy required to recover a mole of

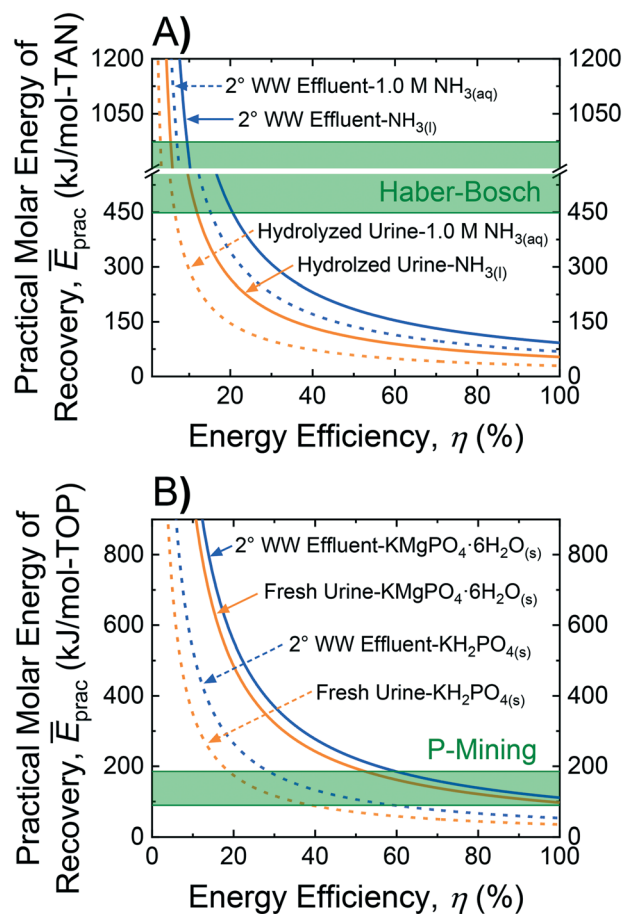


Fig. 7 Practical molar energy, \bar{E}_{prac} as a function of efficiency, η , for an actual process to recover A) TAN from hydrolyzed urine and secondary wastewater effluent as 1.0 M NH_{3(aq)} and NH_{3(l)} and B) TOP from fresh urine and secondary wastewater effluent as KMgPO₄·6H₂O(s) and KH₂PO_{4(s)}. Mid-range \bar{E}_{\min} values were used and $Y \rightarrow 0$, *i.e.*, an infinitesimally small amount of nutrient is recovered from the waste stream, for all scenarios. Note that \bar{E}_{prac} at $\eta = 100\%$ is equivalent to \bar{E}_{\min} . For comparison, the range of energy costs required for N-fixation by the Haber–Bosch process (448–973 kJ mol^{−1})^{1–3} and phosphate rock mining and beneficiation (89–185 kJ mol^{−1})^{5,8} is shown as shaded green areas in A and B, respectively.

nutrient using a putative practical process with an assumed efficiency of η , *i.e.*, $\bar{E}_{\text{prac}} = \bar{E}_{\min}/\eta$. Fig. 7A and B present \bar{E}_{prac} as a function of η for harvesting TAN and TOP products, respectively, from different waste streams. For each nutrient, two products \bar{E}_{\min} were selected to illustrate a range of energy demand, namely pure liquid ammonia and 1.0 M aqueous ammonia solution for N and solid precipitates of potassium magnesium phosphate and potassium phosphate for P. For the waste streams, a centralized source of secondary wastewater effluent and a decentralized source of either hydrolyzed urine or diverted fresh urine for N and P, respectively, were selected for quantitative comparisons. Mid-range \bar{E}_{\min} values from Fig. 3 were used and recovery yield $Y \rightarrow 0$, *i.e.*, an infinitesimally small amount of nutrient is reclaimed from the waste stream. The ranges of energy costs for conventional linear economy approaches to nutrient production, *i.e.*, Haber–

Bosch for N-fixation^{1–3} and mining and beneficiation for phosphate,^{5,8} are also depicted as shaded green regions.

The high energy intensity of nitrogen fixation by the Haber–Bosch process and the relatively low \bar{E}_{\min} signify that TAN recovery from the different waste streams can be competitive across a large range of process efficiencies (lines below the green shaded region of Fig. 7A). Harvesting TAN as 1.0 M $\text{NH}_{3(\text{aq})}$ from hydrolyzed urine requires η as low as $\approx 7\%$ (dashed orange line, Fig. 7A). Even the more energy demanding recovery of $\text{NH}_{3(\text{l})}$ from secondary wastewater effluent can be competitive with separation techniques of efficiencies $>25\%$ (solid blue line). As comparisons, the energy efficiencies of reverse osmosis desalination and liquid–liquid extraction are around 25% (for 10-fold concentration, approximately equivalent to a recovery yield of 0.9).⁹⁵ We note that the \bar{E}_{\min} values utilized for this analysis are for $Y \rightarrow 0$. Even for practical recovery yields $\gg 0$, the elevation of \bar{E}_{\min} is only marginal at most, as previously discussed (Fig. 2 and 5), and, hence, the increase in required energy efficiencies of the actual processes is expected to be modest.

In contrast, the substantially lower energy cost of conventional P production significantly constrains the energy efficiencies for recovery techniques to be competitive. $\text{KH}_2\text{PO}_{4(\text{s})}$ recovery from fresh urine and 2° WW effluent needs η greater than 39% and 59%, respectively, to have lower energy requirements than current phosphate mining and beneficiation (dashed orange and blue lines, Fig. 7B). However, for $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}_{(\text{s})}$ recovery, the energy requirement can, at best, be comparable with the conventional approach for P production, even with highly efficiency methods of $\eta > 60\%$ (solid orange and blue lines). Therefore, the strategic selection of waste stream and nutrient product is imperative to maximize the chances of success for competitive phosphate recovery.

Implications

A circular economy espouses cyclical material flows.⁹⁶ The approach, hence, promotes the recovery of nutrients from discard streams for reuse, to lower industrial N production and P mining from the current unsustainable levels, and concomitantly protect aquatic environments from harmful N and P emissions. To realize viable implementation, the methods for nutrient recovery from waste streams must be competitive with existing practices across key metrics, including energy requirements. This study analyzed the thermodynamics of the separations to identify the minimum energy requirements for various nutrient recovery schemes employing different waste streams as the feed, targeting diverse fertilizer products, and achieving a range of recovery yields. The analysis quantified lower theoretical energy intensities of N and P recovery from nutrient-rich sources, such as diverted fresh and hydrolyzed urine, and indicates that waste stream pH and speciation of components are important factors affecting the separation that need to be considered in the product selection and design of actual

nutrient recovery processes. The analytical approach for thermodynamic evaluation presented here can inform the strategic selection of waste stream, fertilizer product, and recovery yield, to enhance the competitiveness of nutrient recovery on the energy-intensity metric. The specific results and/or the general approach for determination of energy requirements presented here can be employed in life-cycle assessments to more comprehensively evaluate the environmental impacts associated with all the stages of nutrient recovery from waste streams.

The study also sheds light on the potential practical energy requirements of actual nutrient recovery using technologies with various efficiencies. Importantly, the separation processes need to operate above certain efficiencies for energy demand of N and P recoveries to be lower than the conventional linear economy production methods, *i.e.*, Haber–Bosch for N fixation and phosphate rock mining. For instance, ammoniacal nitrogen recovery from hydrolyzed urine, generally the least energy-intensive TAN reclamation among the scenarios investigated here, only requires efficiency $>7\%$. The use of urine as the feed source has additional benefits of reduced pathogen and heavy metal concentrations compared to other waste streams.^{69,97,98} Further, urine contains approximately 80% and 50% of the N and P in human excretions, respectively.^{69,98} Thus, N and P recovery from urine can enable significant reductions in nutrient loading to WWTPs and, ultimately, aquatic environments. Compared to nitrogen recycling, phosphorous reuse is more challenging. Because concentrations in the waste streams are inherently lower and typical fertilizer products are pure solid minerals, the theoretical minimum energy of phosphate recovery is significantly greater. The relatively smaller energy cost of current P mining practices further compounds to the difficulty of the task, necessitating recovery processes to have higher efficiencies in order to be competitive. Technologies with energy efficiencies $>39\%$ are needed even for the least demanding orthophosphate separation and capture from fresh urine. However, with phosphate reserves unceasingly depleting and high-grade ores rapidly exhausted, energy expenditures for mining are expected to surge.^{7,99} Furthermore, nutrient recovery has the additional benefit of environmental protection. Therefore, P recovery from waste streams will likely become increasingly attractive compared to the conventional linear economy approach. Nevertheless, the development of more energy efficient technologies will enhance the accessibility of nutrient recovery from waste streams.

To put in perspective the benefits of a circular economy approach for nutrient management over the existing linear economy model, we performed a first-order estimation of the potential energy savings achievable through supplementing current fertilizer production with nutrient recovery from waste streams. In 2017, the International Fertilizer Association estimated global nutrient demands of 7930×10^9 mol-N and 148×10^9 mol-P.¹⁰⁰ Given the respective concentrations of N and P in hydrolyzed and fresh urine, the world population of 7.6 billion in 2017,¹⁰¹ and 1–2 L d⁻¹ of urine produced per

person, around $748\text{--}3208 \times 10^9$ mol-N and $54\text{--}267 \times 10^9$ mol-P were excreted in urine annually. Therefore, in principle, 9–40% and 36–180% of the N and P fertilizer markets, respectively, could be supplemented by TAN and TOP reclaimed from urine. The recovery of half of the available TAN in hydrolyzed urine as 1.0 M $\text{NH}_{3(\text{aq})}$ using techniques achieving 50% efficiency can notionally reduce the global energy demand for industrial N production by 4.6–20.0%. Similarly, using recovery technologies that are 50% efficient to capture half of the TOP in fresh urine as $\text{KH}_2\text{PO}_{4(\text{s})}$ can presumably reduce the energy required to produce P fertilizer by 4.0–15.9%. The sizable energy savings and significant environmental benefits of capturing N and P from waste streams, particularly urine, for reuse provide compelling justification for the broad implementation of nutrient recovery.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This material is based upon work supported by the National Science Foundation under Grant No. 1903705 and the Science Pathways Scholars Program of Barnard College. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation or Barnard College.

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