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5	Flexible Electrochemical Stripping for Wastewater Ammonia Recovery
6	with Real-Time Product Tunability
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8	Anna Kogler ¹ , Meili Gong ² , William A. Tarpeh ^{1,2*}
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10	¹ Department of Civil and Environmental Engineering, Stanford University, Stanford, CA, 94305, USA
11	² Department of Chemical Engineering, Stanford University, Stanford, CA, 94305, USA
12 13	*Corresponding author, Email: wtarpeh@stanford.edu . Address: 443 Via Ortega, Room 387, Stanford CA, 94305. Telephone: 650-497-1324
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15	
16	Abstract: 179 words
17	Word Count (without figures/tables): 2,385 words
18	Figures: 3 (200 word equivalents each = 600 word equivalents)
19	Word Count: 2,985 words
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Abstract

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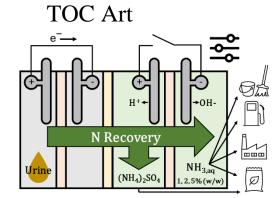
Nitrogen in wastewater can be recovered to prevent negative environmental, human health, and economic impacts and to enable distributed chemical manufacturing. We developed novel flexible electrochemical stripping (FECS) for tunable recovery of ammonia/ammonium (total ammonia nitrogen, TAN) from urine as (NH₄)₂SO₄ and aqueous NH₃. Batch and continuous experiments demonstrated that product speciation could be readily controlled by modifying electrochemical cell operation frequency, duration, and applied current without affecting TAN removal. During continuous experiments, FECS recovered NH₃ solutions with concentrations similar to ready-touse cleaners (1% and 2% NH₃ (w/w) or 8.22 and 16.4 g/L TAN) and cleaner concentrates (5% NH₃ (w/w) or 41.1 g/L TAN), as well as (NH₄)₂SO₄ solutions between 5 and 18.4 g/L TAN, approaching commercial fertilizer concentrations (28.4 g/L TAN). Beyond modifying applied current, future process engineering and operating condition optimization should reduce energy consumption, increase recovery efficiency, and enhance economic viability of FECS. Our findings will enable development and deployment of electrochemical nitrogen recovery in contexts with varying needs for ammonia-based products, paving the way for circular economies that integrate distributed chemical manufacturing with sanitation systems.

Keywords

circular economy, electrodialysis, membrane distillation, nitrogen, product diversification, resource recovery, urine

Statement of Environmental Relevance and Significance

- 42 Tunable electrochemical nitrogen recovery enables distributed manufacturing of ammonia and
- derived products, reducing environmental impacts of wastewater treatment and chemical
- 44 industries.



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1 Introduction

Innovation in wastewater treatment and resource recovery can yield urgently needed solutions that manage humanity's transgression of multiple planetary boundaries (e.g., climate change, nitrogen/phosphorus biochemical flows). 1,2 Traditional wastewater nitrogen removal approaches are energy- and chemical-intensive. Transitioning to wastewater nitrogen recovery can prevent the negative environmental, human health, and economic impacts of nitrogen discharges, 3-5 while reducing greenhouse gas emissions from wastewater treatment⁶ and Haber-Bosch ammonia production⁷ and rebalancing the nitrogen cycle. At the same time, expanding sanitation access requires radical innovations in wastewater management, such as distributed treatment with resource recovery. 8-10 Rapid and transformative innovation enabling resource-efficient wastewater management and circular economies is crucial to preventing irreversible, catastrophic changes around the globe. 11–13 Expanding product portfolios and increasing process tunability can accelerate scale-up and deployment of circular wastewater technologies. Most nitrogen recovery processes generate fertilizer products. 14 Two main challenges associated with recovered fertilizers are their low economic value and the breadth of formulations required to meet variable, regional, and cropspecific needs.^{9,15–17} Co-generating multiple products can improve the economic viability of

recovery technologies. 18-20 Some nitrogen recovery processes co-generate fertilizers and non-

nutrient products, such as fuel (e.g., H₂, ²¹⁻²⁴ CH₄ ^{25,26}), electricity, ^{21,25,27,28} caustic solutions, ²⁵ acids, ²³ H₂O₂, ^{18,25} organics, ^{25,26} and clean water. ^{29,30} Multi-process systems have also been demonstrated to generate multiple separate fertilizer products (e.g., struvite, (NH₄)₂SO₄, potash).³¹ However, recovering non-fertilizer nitrogen products (e.g., microbial protein for use as animal feed²²) and controlling generation of multiple nitrogen products in a single reactor remain underexplored. These advances could facilitate tailoring fertilizer formulations to soil or crop characteristics,³² create more opportunities for nitrogen recovery (e.g., when fertilizer demand is low), and enable recovery of higher-value products. For example, a process that can switch between generating (NH₄)₂SO₄ and NH₃ could have advantages for economic viability and equitable resource access. While (NH₄)₂SO₄ is primarily used as a fertilizer, ³³ NH₃ is not only a fertilizer³⁴ but also a disinfectant, ^{35–38} precursor in chemical synthesis (e.g., plastics), ³⁴ and fuel. ^{39,40} While the price of NH₃ is similar to or lower than that of (NH₄)₂SO₄, products made from NH₃ (e.g., acrylonitrile, hexamethylenediamine, caprolactam) are significantly higher-value (Figure S1-1, Table S1-1). Real-time tunability of product identity and composition can enable distributed applications by responding to changes in product users' needs.^{20,41} Electrochemical processes, which are modular and easily scalable, automatable, low in chemical inputs, and wellsuited for decentralized wastewater treatment and chemical production, ^{16,42–44} can facilitate tunable multi-product recovery that meets specific chemical, public health, and environmental needs. 16 In this study, we demonstrated tunable recovery of wastewater total ammonia nitrogen (TAN, sum of NH₃ and NH₄⁺) as two products – (NH₄)₂SO₄ and aqueous ammonia (NH_{3(aq)}) – in a single flexible electrochemical stripping (FECS) reactor. FECS builds on previously reported electrochemical stripping (ECS, which recovers (NH₄)₂SO₄)⁴⁵⁻⁴⁷ to broaden the TAN product portfolio without dramatically increasing reactor footprint. The specific objectives of this study

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were to: (1) develop a novel reactor architecture for producing two separate ammonia-based products in a single reactor; (2) investigate electrochemical operating parameters as a mechanism for controlling product distribution; and (3) demonstrate continuous urine treatment for tunable generation of multiple commercially relevant aqueous ammonia product solutions. In the fourchambered FECS reactor consisting of two electrochemical cells, the operating frequency and current density of the second electrochemical cell controlled product distribution between (NH₄)₂SO₄ and NH_{3(aq)}. Stable, continuous FECS operation treating urine for 16 days generated 1% and 2% (w/w) NH₃ solutions (8.22 and 16.4 g/L TAN) as ready-to-use cleaners and almost 5% (w/w) NH₃ solution (41.1 g/L TAN) as a cleaner concentrate, in addition to up to 18.4 g/L TAN (NH₄)₂SO₄ fertilizer. Therefore, FECS achieved product diversification beyond fertilizer by recovering two ammonia-based products and enabled tuning product speciation to meet contextspecific needs. With these advances, FECS can facilitate distributed sanitation and manufacturing of NH_{3(aq)} and chemicals derived from it, reducing the environmental impacts of both industries, fostering more equitable access to resources, 48,49 and promoting waste valorization as a strategy to keep human development within planetary limits.⁵⁰

2 Materials and Methods

104 2.1 Urine Collection

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Urine was collected from July 3, 2021 to February 9, 2022 at Stanford University's Shriram Center with approximately equal volumetric contributions from adult male and female donors (Internal Review Board Protocol 60601). Urine was stored in a closed container at room temperature (25°C) and allowed to hydrolyze for at least 12 months. Hydrolyzed urine contained below 0.35 mM urea-N compared to 306 ± 13 mM TAN for batch experiments (Section 2.2) and 353 ± 20 mM TAN for continuous experiments (Section 2.3), indicating complete hydrolysis.

2.2 Controlling Product Speciation with Electrochemical Operation

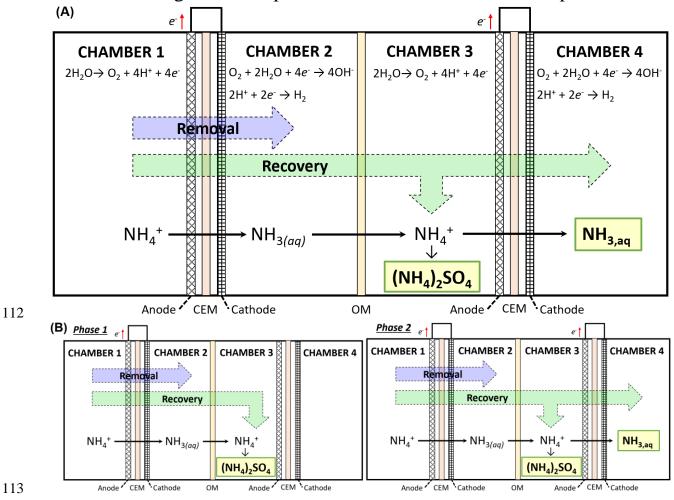


Figure 1. Flexible electrochemical stripping (FECS) process schematic with (A) concurrent electrochemical operation and (B) staggered electrochemical operation. Schematics illustrating flow configuration in batch and continuous experiments are shown in Figure S2-1.

FECS experiments were performed in a four-chambered reactor (Figure 1, Figure S2-1, Table S2-1, Section S2.1). 12-hour batch experiments treating urine (Table S2-2) were conducted in two modes – concurrent (Figure 1A) and staggered (Figure 1B). Staggered experiments were conducted at three currents: 0.64 A (i.e., current density of 100 A/m²), 2 A (i.e., 312.5 A/m²), and 4 A (i.e., 625 A/m²). Experimental details are described in Section S2.2 and analytical procedures

- in Section S2.4. Process performance was evaluated by removal and recovery efficiency and 122
- energy consumption for removal and recovery (Table S2-4, Equations S5-2 to S5-9). 123
- 2.3 Continuous Operation for Tunable Product Generation 124
- A continuous FECS experiment treating urine (Table S2-3) in staggered mode was conducted for 125
- 16 days as described in Section S2.3 (Figure S2-1B through Figure S2-3). We evaluated the 126
- process based on removal and recovery efficiency and energy consumption for removal and 127
- 128 recovery (Table S2-4, Equations S5-10 to S5-23).
- 3 Results and Discussion 129
- 3.1 Controlling Product Speciation with Electrochemical Operation 130
- FECS recovered both NH_{3(aq)} and (NH₄)₂SO₄ from urine containing 4.29 ± 0.19 g/L TAN during 131
- batch experiments. Modifying operation of the second electrochemical cell enabled tuning product 132
- 133 speciation (Figure 2). TAN removal and total TAN recovery were similar for concurrent and
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- staggered operation at 0.64 A (100 A/m²) (Figure 2A, Table S3-1). The product distribution was
- similar for both modes when the second electrochemical cell was on; (NH₄)₂SO₄ in Chamber 3 135
- 136 dominated with $46.4 \pm 9.1\%$ recovery efficiency for $(NH_4)_2SO_4$ and $30.6 \pm 6.6\%$ for $NH_{3(aq)}$ after
- 137 12 hours (2.15 \pm 0.33 g/L TAN as (NH₄)₂SO₄ vs. 1.42 \pm 0.34 g/L TAN as NH_{3(aq)}). Longer
- operation up to 24 hours did not shift product speciation toward NH_{3(aq)} (Figure S3-1, Figure S3-138
- 139 2). While concurrent operation recovered a combination of (NH₄)₂SO₄ and NH_{3(aq)} at all times,
- 140 staggered operation at 0.64 A recovered only (NH₄)₂SO₄ when the second electrochemical cell
- was off (first 6 hours, $75.4 \pm 7.0\%$ recovery efficiency for $(NH_4)_2SO_4$ vs. $0.68 \pm 0.3\%$ for $NH_{3(aq)}$). 141
- Because staggered operation at 0.64 A facilitated control over the start of NH_{3(aq)} recovery (i.e., by 142
- turning on the second electrochemical cell) but still primarily recovered (NH₄)₂SO₄, further 143

modified staggered operation of the second electrochemical cell was needed to target more tunable
 TAN recovery.
 Changing the current applied to the second electrochemical cell influenced product distribution

Changing the current applied to the second electrochemical cell influenced product distribution (Figure 2B). Across three applied currents (0.64 A or 100 A/m², 2 A or 312.5 A/m², and 4 A or 625 A/m²), we observed consistent removal efficiency (Table S3-2), indicating that operation of the second electrochemical cell did not affect the removal process occurring in the first electrochemical cell. Total recovery efficiency was also similar across the three staggered conditions (Table S3-2) except when TAN mass balance closure differed (Figure S3-3). (NH₄)₂SO₄ was the dominant product after 6 hours in all cases, but after 12 hours, the ratio of NH_{3(aq)} to (NH₄)₂SO₄ varied directly with applied current. In fact, NH_{3(aq)} was the dominant product within 2 hours of turning on the second electrochemical cell (8 hours of total operation) at 2 A and 4 A. After 12 hours, recovery efficiencies were 57.1 \pm 7.6% as NH_{3(aq)} versus 17.5 \pm 3.1% as (NH₄)₂SO₄ at 2 A and 65.9 \pm 1.9% as NH_{3(aq)} versus 14.2 \pm 1.9% as (NH₄)₂SO₄ at 4 A. Therefore, increasing current applied to the second electrochemical cell relative to the first cell prioritized NH_{3(aq)} over (NH₄)₂SO₄ production, enabling applications of recovered TAN beyond fertilizer.

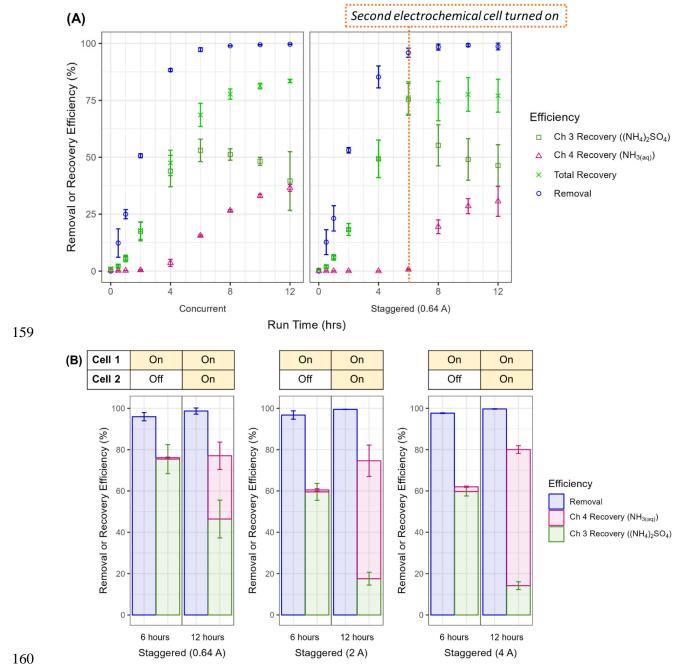


Figure 2. Batch flexible electrochemical stripping (FECS) experiments treating urine using concurrent and staggered electrochemical operation. (A) Removal and recovery efficiency over time during concurrent and staggered operation with the second electrochemical cell operating at 0.64 A. Figure S3-1 shows removal and recovery efficiency for 24-hour experiments in concurrent mode and staggered mode at 0.64 A. (B) Removal and recovery efficiency during staggered operation at different currents. Performance at 6 hours represents the end of Phase 1 of staggered operation when only electrochemical cell 1 is on; data at 12 hours illustrate performance at the end of Phase 2 when both cells are on. The grid above the plots indicates which electrochemical cells are on at the time points shown.

3.2 Continuous Operation for Tunable Product Generation

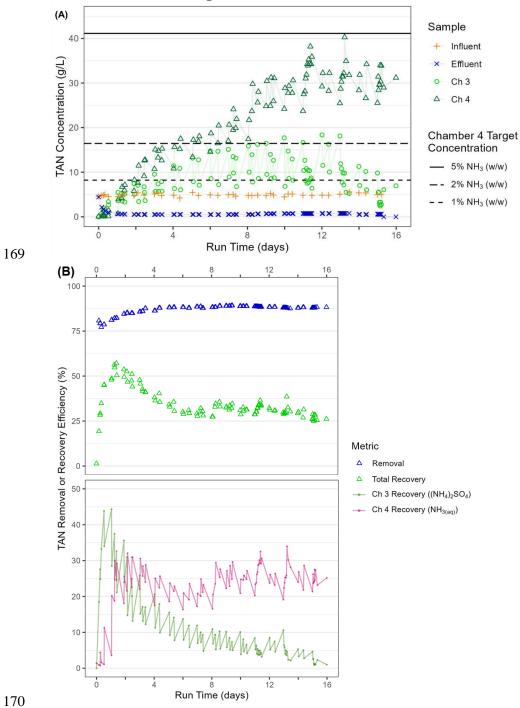


Figure 3. Performance of continuous flexible electrochemical stripping (FECS) with staggered electrochemical cell operation while treating urine. (A) Total ammonia nitrogen (TAN) concentrations over time. (B) Removal efficiency, total recovery efficiency, and recovery efficiency as (NH₄)₂SO₄ in Chamber 3 and NH_{3(aq)} in Chamber 4. Recovery efficiencies shown in panel B consider

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only TAN present in the reactor chambers and recirculation bottles; Figure S3-4 shows analogous metrics accounting for TAN captured in acid traps as well as TAN present in the reactor chambers and recirculation bottles.

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When treating hydrolyzed urine, FECS generated: (1) NH_{3(aq)} in Chamber 4 with concentrations similar to ready-to-use cleaners (1% and 2% NH₃ (w/w)) and cleaner concentrates (5% NH₃ (w/w)) and (2) (NH₄)₂SO₄ solutions in Chamber 3 with no less than 5 g/L TAN and up to 18.4 g/L TAN, approaching commercial fertilizer concentrations (28.4 g/L TAN)⁵¹ (Figure 3). In this study, we prioritized TAN up-concentration into NH₃ solutions over (NH₄)₂SO₄ to advance tunable FECS product distribution compared to previous ECS studies focused on (NH₄)₂SO₄ recovery.⁴⁷ Continuous FECS removed $88.1 \pm 0.72\%$ of TAN from urine with an influent concentration of $4,950 \pm 290$ mg/L TAN (effluent composition shown in Table S3-3). Although continuous FECS achieved removal similar to ECS (83.4 \pm 1.5%), 47 the steady-state recovery efficiency (30.7 \pm 2.8% at 5 days onward) was lower than for ECS $(73.0 \pm 2.9\%)^{47}$ and lower than removal in FECS. Fluctuating pH in Chamber 3 decreased recovery efficiency in FECS compared to ECS by causing an inconsistent NH₃ concentration gradient driving diffusion from Chamber 2 to 3 and thus, TAN accumulation in Chamber 2 (Figure S3-4, Figure S3-5Error! Reference source not found.). Given alkaline conditions in Chambers 3 and 4 (Figure S3-4; intermittently alkaline in Chamber 3, always alkaline in Chamber 4), better sealing these chambers would reduce NH₃ transfer to acid traps and improve recovery efficiency (46.5 \pm 3.3%, Figure S3-6). Additional factors contributing to low FECS recovery included (Figure S3-7 through Figure S3-9, Section S3.2.1): TAN transfer to the Chamber 2 acid trap; TAN oxidation to NO₂, NO₃, and possibly un-measured gaseous species (e.g., N₂); potential losses due to NH₃ volatilization; and possible interference of mesh supports around the omniphobic membrane with TAN mass transfer to and through the membrane. While FECS achieved steady TAN removal and recovery, future improvements are needed to

increase TAN recovery as (NH₄)₂SO₄ and NH_{3(aq)} (e.g., preventing TAN oxidation) or enable recovery of additional products (e.g., gaseous NH₃, NO₃⁻).

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Despite low recovery efficiency, TAN concentrations in Chambers 3 and 4 generally increased over time, and TAN concentrations and product distribution between Chambers 3 and 4 showed short-term fluctuations that reflected operation of the second electrochemical cell (Figure 3). When the second electrochemical cell was on, the TAN concentration in Chamber 3 decreased and the TAN concentration in Chamber 4 increased due to electromigration of NH₄⁺ from Chamber 3 to 4. When the second electrochemical cell was off, the TAN concentration in Chamber 4 decreased and the TAN concentration in Chamber 3 increased due to NH₃ back-diffusion from Chamber 4 to 3. Chamber 4 TAN concentration seemed to plateau (i.e., fluctuated between 23.7 and 31.2 g/L each day) starting at about 8 days. On Days 11 and 13, we achieved higher Chamber 4 concentrations (up to 40.3 g/L TAN, 4.89% NH₃ (w/w)) and greater product distribution toward NH_{3(aq)} over (NH₄)₂SO₄ by increasing the operation frequency of the second electrochemical cell (i.e., 1-hour on vs. 1-hour off periods instead of 1-hour on vs. 6- to 12-hour off periods) to limit back-diffusion (Figure S3-10). Reactor modifications (e.g., using a thicker CEM in the second electrochemical cell,⁵² alternative architectures like electrocatalyst-in-a-box (ECaB)⁵³) in combination with the demonstrated operational strategy could further enhance NH_{3(aq)} recovery. Long-term FECS operation revealed water transfer from Chamber 3 to 4 (due to osmosis and electro-osmosis) as a second challenge to $NH_{3(aq)}$ up-concentration (Figure S3-11, Figure S3-12). While water transfer did not drastically affect the time needed to reach ready-to-use cleaner concentrations (1% and 2% (w/w) NH₃), reaching 5% (w/w) NH₃ could have been achieved in 9.4 rather than 13.2 days without water transfer (Figure S3-13). This detrimental effect of water transfer was most noticeable at the highest target concentration because greater concentration

differences across the second CEM resulted in more osmotic water transport.^{54,55} Mitigating water transfer likely requires material innovations, like tuning membrane properties (e.g., polymer and fixed charge group identity, pore size and connectivity, coating). 56-58 Therefore, integrated optimization of reactor architecture, materials, and operation is needed to achieve more complete TAN recovery and higher $NH_{3(aq)}$ concentrations in FECS. The tunability that FECS offers had significant energy and monetary costs (Figure S3-14). TAN removal via FECS required about 166 ± 8.2 MJ/kg N compared to 61.2 ± 4.2 MJ/kg N for ECS.⁴⁷ Energy consumption for recovery was 470 \pm 56 MJ/kg N compared to 69.6 \pm 3.2 MJ/kg N recovered for ECS, 47 32 MJ/kg N for conventional ammonia stripping, 59 31.6 MJ/kg N for the Haber-Bosch process, 60 and 77.9 MJ/kg N for conventional nitrogen management via the Haber-Bosch process and nitrification-denitrification (Figure S3-15, Table S3-4). ^{46,60} Despite the high energy demand of FECS, in situ acid and base generation minimized chemical inputs, which can contribute significantly to life-cycle costs and environmental impacts for nitrogen recovery technologies.⁶¹ Each electrochemical cell contributed almost equally to total energy consumption (Figure S3-16). Modifying the applied current for the second electrochemical cell could reduce energy demand (Figure S3-17, Figure S3-18, Table S3-5, Table S3-6, Section S3.2.2). Altering the operation frequency of the second electrochemical cell and reactor architecture could improve energy efficiency by maintaining more consistent migration from Chamber 2 to 3 and reducing NH₃ back-diffusion from Chamber 4 to 3. Additional energy consumption and reactor components (e.g., two anodes in FECS vs. one in ECS⁴⁷) entail significant costs for the additional functionality that FECS enables, motivating future studies on low-cost, durable materials; alternative reactor configurations that reduce TAN losses and increase recovery efficiency; and further tuning

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operating parameters to reduce energy consumption, improve recovery, and enhance product control.

4 Implications

We demonstrated a novel reactor, FECS, that facilitates tunable recovery of ammonia/ammonium from urine as both (NH₄)₂SO₄ and NH_{3(aq)}. While (NH₄)₂SO₄ is mainly used as a fertilizer, NH₃ is more versatile, with uses as a disinfecting cleaner, ^{35–38} green fuel, ^{39,40} and industrial feedstock for plastic, rubber, and fiber synthesis. ³⁴ With minimal chemical inputs and real-time control over product distribution, FECS can integrate distributed wastewater treatment and chemical manufacturing in diverse settings with changing local needs and markets. Simpler, lower-cost, and lower-energy systems like ECS may be more suitable in cases where TAN removal is the primary goal (e.g., due to regulatory limits on environmental discharges). However, FECS is valuable if NH_{3(aq)} or switching between (NH₄)₂SO₄ and NH_{3(aq)} is desirable. For instance, FECS could supply NH₃ to nearby industries reducing dependence on long-distance supply chains and provide both fertilizers and cleaners to remote rural agricultural communities. Therefore, integrating FECS into sanitation systems can promote more equitable resource access, improve food security and health, and lower environmental impacts of chemical industries while contributing to re-engineering the nitrogen cycle toward circularity.

Supporting Information

The supporting information includes text describing reactor setup and operation; tables describing influent and effluent streams, reactor component properties, statistical analysis of performance metrics, and product prices; equations for efficiencies and energy demand; and figures showing reactor setup, temporal trends in performance metrics and composition, and product prices.

Acknowledgements

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265 We thank the Tarpeh lab for productive discussions in developing this work. The project was funded by the Stanford University King Center on Global Development, Stanford University 266 267 Center for Innovation in Global Health, and the Sustainability Accelerator from the Stanford Doerr School of Sustainability. Authors also acknowledge the following additional support: AK – 268 Stanford University Vice Provost for Graduate Education; MG – National Alliance for Water 269 Innovation (NAWI); and WAT – Camille and Henry Dreyfus Foundation. NAWI is funded by the 270 U.S. Department of Energy, Energy Efficiency and Renewable Energy Office, Advanced 271 Manufacturing Office under Funding Opportunity Announcement DE-FOA-0001905. Funding 272 273 has been provided in full or in part through an agreement with the California State Water Resources Control Board using funds from Proposition 1. The contents of this document do not necessarily 274 reflect the views and policies of the foregoing, nor does mention of trade names or commercial 275 276 products constitute endorsement or recommendation for use.

References

- (1) Rockström, J.; Steffen, W.; Noone, K.; Persson, Å.; Chapin, F. S.; Lambin, E. F.; Lenton, T. M.;
 Scheffer, M.; Folke, C.; Schellnhuber, H. J.; Nykvist, B.; De Wit, C. A.; Hughes, T.; Van Der Leeuw,
 S.; Rodhe, H.; Sörlin, S.; Snyder, P. K.; Costanza, R.; Svedin, U.; Falkenmark, M.; Karlberg, L.;
 Corell, R. W.; Fabry, V. J.; Hansen, J.; Walker, B.; Liverman, D.; Richardson, K.; Crutzen, P.; Foley,
 J. A. A Safe Operating Space for Humanity. *Nature* 2009, 461 (7263), 472–475.
 https://doi.org/10.1038/461472a.
- (2) Steffen, W.; Richardson, K.; Rockström, J.; Cornell, S. E.; Fetzer, I.; Bennett, E. M.; Biggs, R.;
 Carpenter, S. R.; de Vries, W.; de Wit, C. A.; Folke, C.; Gerten, D.; Heinke, J.; Mace, G. M.;
 Persson, L. M.; Ramanathan, V.; Reyers, B.; Sörlin, S. Planetary Boundaries: Guiding Human
 Development on a Changing Planet. *Science* 2015, 347 (6223), 1259855.
 https://doi.org/10.1126/science.1259855.
- (3) Dodds, W. K.; Bouska, W. W.; Eitzmann, J. L.; Pilger, T. J.; Pitts, K. L.; Riley, A. J.; Schloesser, J.
 T.; Thornbrugh, D. J. Eutrophication of U.S. Freshwaters: Analysis of Potential Economic Damages.
 Environ. Sci. Technol. 2009, 43 (1), 12–19. https://doi.org/10.1021/es801217q.
- 292 (4) Burow, K. R.; Nolan, B. T.; Rupert, M. G.; Dubrovsky, N. M. Nitrate in Groundwater of the United
 293 States, 1991–2003. *Environ. Sci. Technol.* 2010, 44 (13), 4988–4997.
 294 https://doi.org/10.1021/es100546y.
- (5) Falconer, I. R. An Overview of Problems Caused by Toxic Blue–Green Algae (Cyanobacteria) in
 Drinking and Recreational Water. *Environmental Toxicology* 1999, 14 (1), 5–12.
 https://doi.org/10.1002/(SICI)1522-7278(199902)14:1<5::AID-TOX3>3.0.CO;2-0.

- 298 (6) Juli Iacuaniello; Orianna Bretschger. Decentralizing wastewater treatment can help corporations
 299 achieve climate goals. World Economic Forum.
- https://www.weforum.org/agenda/2022/10/wastewater-corporations-climate-goals/ (accessed 2024-01-09).
- 302 (7) Kyriakou, V.; Garagounis, I.; Vourros, A.; Vasileiou, E.; Stoukides, M. An Electrochemical Haber-303 Bosch Process. *Joule* **2020**, *4* (1), 142–158. https://doi.org/10.1016/j.joule.2019.10.006.
- 304 (8) Larsen, T. A.; Hoffmann, S.; Lüthi, C.; Truffer, B.; Maurer, M. Emerging Solutions to the Water Challenges of an Urbanizing World. *Science* **2016**, *352* (6288), 928–933.
- (9) Larsen, T. A.; Gruendl, H.; Binz, C. The Potential Contribution of Urine Source Separation to the
 SDG Agenda a Review of the Progress so Far and Future Development Options. *Environ. Sci.:* Water Res. Technol. 2021, 7 (7), 1161–1176. https://doi.org/10.1039/D0EW01064B.
- 309 (10) Randall, D. G.; Naidoo, V. Urine: The Liquid Gold of Wastewater. *Journal of Environmental Chemical Engineering* **2018**, *6* (2), 2627–2635. https://doi.org/10.1016/j.jece.2018.04.012.
- (11) Will Steffen; Angelina Sanderson; Peter Tyson; Jill Jaeger; Pamela Matson; Berrien Moore III; Frank
 Oldfield; Katherine Richardson; H. John Schellnhuber; B.L. Turner II; Robert J. Wasson. *Global* Change and the Earth System: A Planet Under Pressure, 2nd printing.; Springer-Verlag: Berlin,
 2005.
- (12) Lenton, T. M.; Held, H.; Kriegler, E.; Hall, J. W.; Lucht, W.; Rahmstorf, S.; Schellnhuber, H. J.
 Tipping Elements in the Earth's Climate System. *Proc. Natl. Acad. Sci. U.S.A.* 2008, *105* (6), 1786–1793. https://doi.org/10.1073/pnas.0705414105.
- 318 (13) Scheffer, M.; Carpenter, S.; Foley, J. A.; Folke, C.; Walker, B. Catastrophic Shifts in Ecosystems. 319 *Nature* **2001**, *413* (6856), 591–596. https://doi.org/10.1038/35098000.
- (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 EST Eng. 2021, 1 (4), 662–684.
 https://doi.org/10.1021/acsestengg.0c00253.

328

- (15)J.R. McConville; E. Kvarnström; H. Jönsson; E. Kärrman; M. Johansson. Is the Swedish Wastewater
 Sector Ready for a Transition to Source Separation? *dwt* 2017, *91*, 320–328.
 https://doi.org/10.5004/dwt.2017.20881.
 - (16)Miller, D. M.; Abels, K.; Guo, J.; Williams, K. S.; Liu, M. J.; Tarpeh, W. A. Electrochemical Wastewater Refining: A Vision for Circular Chemical Manufacturing. *J. Am. Chem. Soc.* **2023**. https://doi.org/10.1021/jacs.3c01142.
- (17) Hengl, T.; Leenaars, J. G. B.; Shepherd, K. D.; Walsh, M. G.; Heuvelink, G. B. M.; Mamo, T.;
 Tilahun, H.; Berkhout, E.; Cooper, M.; Fegraus, E.; Wheeler, I.; Kwabena, N. A. Soil Nutrient Maps of Sub-Saharan Africa: Assessment of Soil Nutrient Content at 250 m Spatial Resolution Using Machine Learning. *Nutr Cycl Agroecosyst* 2017, *109* (1), 77–102. https://doi.org/10.1007/s10705-017-9870-x.
- (18) Wang, R.; Yang, K.; Wong, C.; Aguirre-Villegas, H.; Larson, R.; Brushett, F.; Qin, M.; Jin, S.
 Electrochemical Ammonia Recovery and Co-Production of Chemicals from Manure Wastewater. *Nat Sustain* 2023, 1–12. https://doi.org/10.1038/s41893-023-01252-z.
- (19) Mousset, E.; Fournier, M.; Su, X. Recent Advances of Reactive Electroseparation Systems for Water
 Treatment and Selective Resource Recovery. *Current Opinion in Electrochemistry* 2023, 42, 101384.
 https://doi.org/10.1016/j.coelec.2023.101384.
- (20) Pickett, M. T.; Roberson, L. B.; Calabria, J. L.; Bullard, T. J.; Turner, G.; Yeh, D. H. Regenerative
 Water Purification for Space Applications: Needs, Challenges, and Technologies towards "Closing
 the Loop." *Life Sciences in Space Research* 2020, 24, 64–82.
 https://doi.org/10.1016/j.lssr.2019.10.002.
- (21) Ledezma, P.; Kuntke, P.; Buisman, C. J. N.; Keller, J.; Freguia, S. Source-Separated Urine Opens
 Golden Opportunities for Microbial Electrochemical Technologies. *Trends in Biotechnology* 2015, *33* (4), 214–220. https://doi.org/10.1016/j.tibtech.2015.01.007.

- 348 (22) Christiaens, M. E. R.; Udert, K. M.; Arends, J. B. A.; Huysman, S.; Vanhaecke, L.; McAdam, E.; 349 Rabaey, K. Membrane Stripping Enables Effective Electrochemical Ammonia Recovery from Urine While Retaining Microorganisms and Micropollutants. Water Research 2019, 150, 349–357. 350 351 https://doi.org/10.1016/j.watres.2018.11.072.
- (23) Zhang, Y.; Angelidaki, I. Recovery of Ammonia and Sulfate from Waste Streams and Bioenergy 352 Production via Bipolar Bioelectrodialysis. Water Research 2015, 85, 177–184. 353 354 https://doi.org/10.1016/j.watres.2015.08.032.
- 355 (24) Xie, A.; Popat, S. C. Electrochemical Ammonia Stripping from Non-Nitrified Animal Rendering 356 Wastewater. Chemical Engineering Journal Advances 2020, 3, 100020. https://doi.org/10.1016/j.ceja.2020.100020. 357
- (25)Logan, B. E.; Rabaey, K. Conversion of Wastes into Bioelectricity and Chemicals by Using 358 Microbial Electrochemical Technologies. Science 2012, 337 (6095), 686-690. 359 360 https://doi.org/10.1126/science.1217412.

368

- (26) Nidheesh, P. V.; Ganiyu, S. O.; Kuppam, C.; Mousset, E.; Samsudeen, N.; Olvera-Vargas, H.; 361 Kumar, G. Bioelectrochemical Cells as a Green Energy Source for Electrochemical Treatment of 362 Water and Wastewater. Journal of Water Process Engineering 2022, 50, 103232. 363 https://doi.org/10.1016/j.jwpe.2022.103232. 364
- 365 (27) Kuntke, P.; Śmiech, K. M.; Bruning, H.; Zeeman, G.; Saakes, M.; Sleutels, T. H. J. A.; Hamelers, H. V. M.; Buisman, C. J. N. Ammonium Recovery and Energy Production from Urine by a Microbial 366 Fuel Cell. Water Research 2012, 46 (8), 2627–2636. https://doi.org/10.1016/j.watres.2012.02.025.
 - (28) Koskue, V.; Rinta-Kanto, J. M.; Freguia, S.; Ledezma, P.; Kokko, M. Optimising Nitrogen Recovery from Reject Water in a 3-Chamber Bioelectroconcentration Cell. Separation and Purification Technology **2021**, 264, 118428. https://doi.org/10.1016/j.seppur.2021.118428.
- (29) Sutherland, D. L.; Turnbull, M. H.; Craggs, R. J. Increased Pond Depth Improves Algal Productivity 371 and Nutrient Removal in Wastewater Treatment High Rate Algal Ponds. Water Research 2014, 53, 372 373 271–281. https://doi.org/10.1016/j.watres.2014.01.025.
- 374 (30) Xie, M.; Nghiem, L. D.; Price, W. E.; Elimelech, M. Toward Resource Recovery from Wastewater: 375 Extraction of Phosphorus from Digested Sludge Using a Hybrid Forward Osmosis-Membrane 376 Distillation Process. Environ. Sci. Technol. Lett. 2014, 1 (2), 191–195. 377 https://doi.org/10.1021/ez400189z.
- 378 (31) Jagtap, N.; Boyer, T. H. Integrated, Multi-Process Approach to Total Nutrient Recovery from Stored 379 Urine. Environ. Sci.: Water Res. Technol. 2018, 4 (10), 1639–1650. 380 https://doi.org/10.1039/C8EW00004B.
- 381 (32) Trimmer, J. T.; Margenot, A. J.; Cusick, R. D.; Guest, J. S. Aligning Product Chemistry and Soil Context for Agronomic Reuse of Human-Derived Resources. Environ. Sci. Technol. 2019, 53 (11), 382 383 6501–6510. https://doi.org/10.1021/acs.est.9b00504.
- 384 (33) Speight, J. G. Chapter Three - Industrial Inorganic Chemistry. In Environmental Inorganic Chemistry 385 for Engineers; Speight, J. G., Ed.; Butterworth-Heinemann, 2017; pp 111–169. 386 https://doi.org/10.1016/B978-0-12-849891-0.00003-5.
- 387 (34) International Energy Agency. Ammonia Technology Roadmap: Towards More Sustainable Nitrogen 388 Fertiliser Production; OECD, 2021. https://doi.org/10.1787/f6daa4a0-en.
- 389 (35) Ogunyoku, T. A.; Habebo, F.; Nelson, K. L. In-Toilet Disinfection of Fresh Fecal Sludge with 390 Ammonia Naturally Present in Excreta. Journal of Water, Sanitation and Hygiene for Development 391 **2016**, 6 (1), 104–114. https://doi.org/10.2166/washdev.2015.233.
- 392 (36) Decrey, L.; Kazama, S.; Udert, K. M.; Kohn, T. Ammonia as an In Situ Sanitizer: Inactivation 393 Kinetics and Mechanisms of the ssRNA Virus MS2 by NH₃. Environ. Sci. Technol. 2015, 49 (2), 394 1060-1067. https://doi.org/10.1021/es5044529.
- (37) Pecson, B. M.; Nelson, K. L. Inactivation of Ascaris Suum Eggs by Ammonia. Environ. Sci. Technol. 395 396 **2005**, 39 (20), 7909–7914. https://doi.org/10.1021/es050659a.
- 397 (38) Jenkins, M. B.; Bowman, D. D.; Ghiorse, W. C. Inactivation of Cryptosporidium Parvum Oocysts by 398 Ammonia. Appl Environ Microbiol 1998, 64 (2), 784–788.

- 399 (39)MacFarlane, D. R.; Cherepanov, P. V.; Choi, J.; Suryanto, B. H. R.; Hodgetts, R. Y.; Bakker, J. M.; Ferrero Vallana, F. M.; Simonov, A. N. A Roadmap to the Ammonia Economy. *Joule* **2020**, *4* (6), 1186–1205. https://doi.org/10.1016/j.joule.2020.04.004.
- 402 (40) Valera-Medina, A.; Amer-Hatem, F.; Azad, A. K.; Dedoussi, I. C.; de Joannon, M.; Fernandes, R. X.;
 403 Glarborg, P.; Hashemi, H.; He, X.; Mashruk, S.; McGowan, J.; Mounaim-Rouselle, C.; Ortiz-Prado,
 404 A.; Ortiz-Valera, A.; Rossetti, I.; Shu, B.; Yehia, M.; Xiao, H.; Costa, M. Review on Ammonia as a
 405 Potential Fuel: From Synthesis to Economics. *Energy Fuels* 2021, 35 (9), 6964–7029.
 406 https://doi.org/10.1021/acs.energyfuels.0c03685.
- 407 (41) Tarpeh, W. A.; Chen, X. Making Wastewater Obsolete: Selective Separations to Enable Circular Water Treatment. *Environmental Science and Ecotechnology* **2021**, *5*, 100078. https://doi.org/10.1016/j.ese.2021.100078.
- 410 (42) Chaplin, B. P. The Prospect of Electrochemical Technologies Advancing Worldwide Water 411 Treatment. *Acc. Chem. Res.* **2019**, *52* (3), 596–604. https://doi.org/10.1021/acs.accounts.8b00611.
- 412 (43)Radjenovic, J.; Sedlak, D. L. Challenges and Opportunities for Electrochemical Processes as Next-413 Generation Technologies for the Treatment of Contaminated Water. *Environ. Sci. Technol.* **2015**, 49 414 (19), 11292–11302. https://doi.org/10.1021/acs.est.5b02414.
- (44) Kong, L.; Liu, X. Emerging Electrochemical Processes for Materials Recovery from Wastewater:
 Mechanisms and Prospects. *Front. Environ. Sci. Eng.* 2020, *14* (5), 90.
 https://doi.org/10.1007/s11783-020-1269-2.
- 418 (45) Tarpeh, W. A.; Barazesh, J. M.; Cath, T. Y.; Nelson, K. L. Electrochemical Stripping to Recover 419 Nitrogen from Source-Separated Urine. *Environ. Sci. Technol.* **2018**, *52* (3), 1453–1460. 420 https://doi.org/10.1021/acs.est.7b05488.
- 421 (46)Liu, M. J.; Neo, B. S.; Tarpeh, W. A. Building an Operational Framework for Selective Nitrogen 422 Recovery via Electrochemical Stripping. *Water Research* **2020**, *169*, 115226. 423 https://doi.org/10.1016/j.watres.2019.115226.
- (47) Kogler, A.; Sharma, N.; Tiburcio, D.; Gong, M.; Miller, D. M.; Williams, K. S.; Chen, X.; Tarpeh,
 W. A. Long-Term Robustness and Failure Mechanisms of Electrochemical Stripping for Wastewater
 Ammonia Recovery. ACS Environ. Au 2024, acsenvironau.3c00058.
 https://doi.org/10.1021/acsenvironau.3c00058.
- 428 (48) Comer, B. M.; Fuentes, P.; Dimkpa, C. O.; Liu, Y.-H.; Fernandez, C. A.; Arora, P.; Realff, M.; 429 Singh, U.; Hatzell, M. C.; Medford, A. J. Prospects and Challenges for Solar Fertilizers. *Joule* **2019**, 430 *3* (7), 1578–1605. https://doi.org/10.1016/j.joule.2019.05.001.
- 431 (49)McArthur, J. W.; McCord, G. C. Fertilizing Growth: Agricultural Inputs and Their Effects in Economic Development. *J Dev Econ* **2017**, *127*, 133–152. 433 https://doi.org/10.1016/j.jdeveco.2017.02.007.
- 434 (50)Lim, M. M. L.; Søgaard Jørgensen, P.; Wyborn, C. A. Reframing the Sustainable Development Goals 435 to Achieve Sustainable Development in the Anthropocene - a Systems Approach. *E&S* **2018**, *23* (3), 436 art22. https://doi.org/10.5751/ES-10182-230322.
- 437 (51)Rodrigues, M.; Lund, R. J.; ter Heijne, A.; Sleutels, T.; Buisman, C. J. N.; Kuntke, P. Application of 438 Ammonium Fertilizers Recovered by an Electrochemical System. *Resources, Conservation and* 439 *Recycling* **2022**, *181*, 106225. https://doi.org/10.1016/j.resconrec.2022.106225.
- (52) Roman, M.; Roman, P.; Verbeke, R.; Gutierrez, L.; Vanoppen, M.; Dickmann, M.; Egger, W.;
 Vankelecom, I.; Post, J.; Cornelissen, E.; Keesman, K.; Verliefde, A. Non-Steady Diffusion and
 Adsorption of Organic Micropollutants in Ion-Exchange Membranes: Effect of the Membrane
 Thickness. *iScience* 2021, 24 (2), 102095. https://doi.org/10.1016/j.isci.2021.102095.
- 444 (53)Miller, D.; Liu, M.; Abels, K.; Kogler, A.; Williams, K.; Tarpeh, W. Engineering a Molecular 445 Electrocatalytic System for Energy-Efficient Ammonia Production from Wastewater Nitrate. 446 ChemRxiv February 8, 2024. https://doi.org/10.26434/chemrxiv-2023-1s6n8-v2.
- 447 (54) Galama, A. H.; Saakes, M.; Bruning, H.; Rijnaarts, H. H. M.; Post, J. W. Seawater Predesalination with Electrodialysis. *Desalination* **2014**, *342*, 61–69. https://doi.org/10.1016/j.desal.2013.07.012.

- (55) Galama, A. H.; Vermaas, D. A.; Veerman, J.; Saakes, M.; Rijnaarts, H. H. M.; Post, J. W.; Nijmeijer,
 K. Membrane Resistance: The Effect of Salinity Gradients over a Cation Exchange Membrane.
 Journal of Membrane Science 2014, 467, 279–291. https://doi.org/10.1016/j.memsci.2014.05.046.
- 452 (56)Kingsbury, R. S.; Zhu, S.; Flotron, S.; Coronell, O. Microstructure Determines Water and Salt 453 Permeation in Commercial Ion-Exchange Membranes. *ACS Appl. Mater. Interfaces* **2018**, *10* (46), 454 39745–39756. https://doi.org/10.1021/acsami.8b14494.
- (57) Rommerskirchen, A.; Roth, H.; Linnartz, C. J.; Egidi, F.; Kneppeck, C.; Roghmans, F.; Wessling, M.
 Mitigating Water Crossover by Crosslinked Coating of Cation-Exchange Membranes for Brine
 Concentration. Advanced Materials Technologies 2021, 6 (10), 2100202.
 https://doi.org/10.1002/admt.202100202.
- 459 (58) Kamcev, J.; Freeman, B. D. Charged Polymer Membranes for Environmental/Energy Applications.

 460 *Annu. Rev. Chem. Biomol. Eng.* **2016**, 7 (1), 111–133. https://doi.org/10.1146/annurev-chembioeng-080615-033533.
- 462 (59) Maurer, M.; Schwegler, P.; Larsen, T. A. Nutrients in Urine: Energetic Aspects of Removal and Recovery. *Water Science and Technology* **2003**, *48* (1), 37–46. https://doi.org/10.2166/wst.2003.0011.
- (60) Rouwenhorst, K. H. R.; Krzywda, P. M.; Benes, N. E.; Mul, G.; Lefferts, L. Chapter 4 Ammonia
 Production Technologies. In *Techno-Economic Challenges of Green Ammonia as an Energy Vector*;
 Valera-Medina, A., Banares-Alcantara, R., Eds.; Academic Press, 2021; pp 41–83.
 https://doi.org/10.1016/B978-0-12-820560-0.00004-7.
- (61) Kavvada, O.; Tarpeh, W. A.; Horvath, A.; Nelson, K. L. Life-Cycle Cost and Environmental
 Assessment of Decentralized Nitrogen Recovery Using Ion Exchange from Source-Separated Urine
 through Spatial Modeling. *Environ. Sci. Technol.* 2017, 51 (21), 12061–12071.
 https://doi.org/10.1021/acs.est.7b02244.