

Reactive Separation of Ammonia from Wastewater Nitrate via Molecular Electrocatalysis

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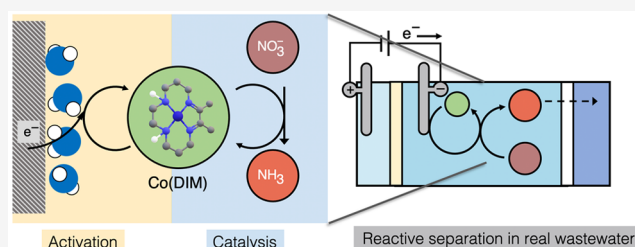
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ABSTRACT: Selective electrochemical conversion of nitrate to ammonia with ammonia capture can simultaneously remediate nitrate-polluted wastewater and supplement Haber-Bosch ammonia production. Homogeneous molecular catalysts remain underexplored in wastewater treatment and, more generally, in reactive separation processes. Despite the tunable reactivity of molecular catalysts, two barriers prevent their widespread implementation for wastewater nitrate treatment and ammonia recovery. The first barrier is the lack of reports of reaction activity and selectivity of nitrate reduction molecular catalysts in real wastewaters. The second barrier is the need to separate the catalyst, catalytic product, and treated wastewater. In this study, we employ electrochemical stripping in several configurations as a reactive separation unit process to address both barriers to implementation. Using the homogeneous molecular nitrate reduction catalyst Co(DIM), we demonstrate >70% removal of nitrate from municipal wastewater treatment plant secondary effluent with >98.5% selectivity to ammonia, leading to the generation of a high-purity ammonia product (ammonium sulfate). These experiments constitute a novel demonstration of molecular catalysis for nitrate reduction in real wastewater and highlight electrochemical engineering opportunities in reactive separations to valorize wastewater resources. This work advances environmental research toward United Nations Sustainable Development Goals (SDGs) for Clean Water (SDG 6) and Responsible Consumption and Production (SDG 12).

KEYWORDS: ammonia synthesis, electrochemical engineering, electrochemical nitrate reduction, reactive nitrogen, resource recovery



1. INTRODUCTION

Anthropogenic perturbations to the global nitrogen cycle have made nitrogen management a looming energy and environmental challenge central to chemical manufacturing and ecosystem protection.^{1,2} Conventional Haber-Bosch (HB) ammonia (NH₃) production requires a high temperature (400 °C), a high pressure (100–200 atm), a large energy input (1–2% of global energy), and a large amount of greenhouse gas emissions (1.2% of anthropogenic CO₂).^{3–5} Ammonium (NH₄⁺) and nitrate (NO₃⁻) comprise roughly equal fractions of aqueous reactive nitrogen pollution and are removed from the environment at a rate slower than the rate of HB production. The continual net discharge of nitrogen exacerbates eutrophication, threatens biodiversity, and skews the nitrogen cycle; damage from the emission of nitrogen to freshwater alone costs billions of dollars annually.^{6,7} As such, the U.S. National Academy of Engineering has deemed managing the nitrogen cycle as a 21st century Grand Challenge for Engineering.⁸ The call to action aligns with the United Nations Sustainable Development Goals 6 (Clean Water and Sanitation) and 12 (Responsible Consumption and Produc-

tion), which seek to ensure sustainable and efficient water and natural resource management, respectively. Electricity-driven processes can contribute to nitrogen production and support the frequently distributed nature of nitrogen pollution.

Selective reduction of nitrate to ammonia with product recovery enables the use of nitrate-rich wastewaters as chemical feedstocks for electrified ammonia production. Nitrate, one of the most prevalent drinking water contaminants,^{6,9} has a relatively low dissociation energy of the N=O bond (204 kJ mol⁻¹) amenable to reduction. However, conversion to ammonia requires eight electron transfers and nine proton transfers, making reaction selectivity a key challenge to the electrochemical nitrate reduction reaction (NO₃RR) in two respects: competition between NO₃RR and the hydrogen

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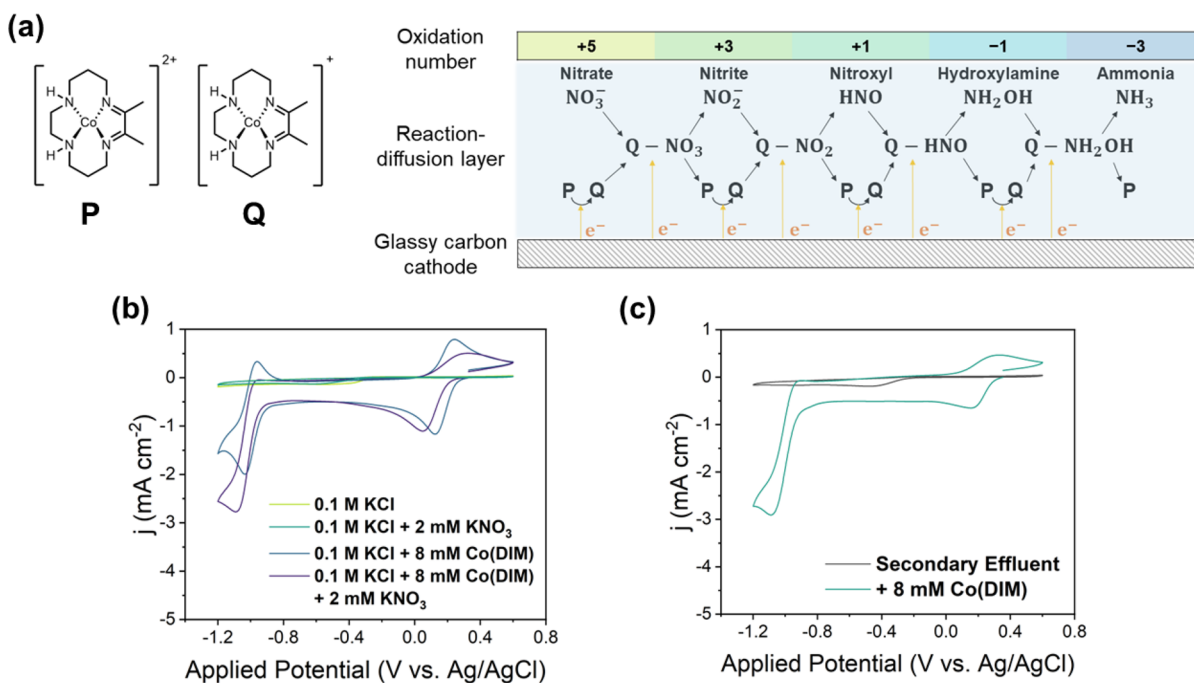


Figure 1. (a) Conversion of nitrate to ammonia in the reaction-diffusion layer and chemical structures of Co(DIM) in precatalytic form (**P**) and active catalytic form (**Q**). The dissociation and coordination of axial bromide or aqua ligands were considered outside of the catalytic cycle, because ligand kinetics are not expected to impact the conversion of nitrate to ammonia.³⁸ *In situ* generation of the catalytically active, low-valence Co species **Q** occurs via the transfer of an electron from the glassy carbon cathode to species **P**. Active catalyst **Q** binds nitrate and facilitates conversion to nitrite. A subsequent cascade of analogous catalytic turnovers converts nitrite to nitroxyl, nitroxyl to hydroxylamine, and hydroxylamine to ammonia. (b) Cyclic voltammograms collected in 0.1 M KCl (supporting salt), 0.1 M KCl with 2 mM KNO₃, 0.1 M KCl with 8 mM Co(DIM), and 0.1 M KCl with 2 mM KNO₃ and 8 mM Co(DIM). Cyclic voltammograms were collected at 100 mV s⁻¹ on a 3 mm diameter glassy carbon disk. (c) Cyclic voltammograms collected in real secondary effluent in the absence or presence of 8 mM Co(DIM). Cyclic voltammograms were collected at 100 mV s⁻¹ on a 3 mm diameter glassy carbon disk.

evolution reaction (HER) and competition between the formation of ammonia and other nitrogenous byproducts (e.g., NO₂⁻ and N₂).^{10–12} Homogeneous molecular catalysts can mediate both selective NO₃RR and NH₃ formation because of the atomically precise coordination of nitrate to catalyst active sites. Despite several NO₃RR molecular catalysts with promising reaction performance,^{13–15} two mechanistic barriers surrounding investigation of catalysis in intended-use wastewaters and reactor architectures have prevented the tunable reactivity of molecular catalysts from being leveraged in wastewater nitrate treatment. The first barrier is the paucity of studies validating NO₃RR molecular catalysts in large-volume, nitrate-rich wastewaters like fertilizer runoff and municipal wastewater effluent (typically <4 mM).^{16–18} Reporting reaction activity and selectivity in the native wastewater environment is necessary to challenge the putative assumption that performance in ideal electrolytes is representative of performance in real wastewaters. We investigate the catalyst Co(DIM) (DIM = 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene), which yields ammonia as the majority catalytic product,¹⁹ for treatment of secondary effluent, which has representative concentrations of nitrate (~2 mM) and inorganic dissolved solids (Table S1).²⁰ The second barrier to implementation, which can be applied to both homogeneous and heterogeneous catalysis, is the development of reactive separations. Although separations and catalysis have been historically viewed and developed separately,^{21,22} the recovery of resources from impaired feedstocks such as wastewaters motivates the co-location and co-investigation of selective reactions with selective separa-

tions.^{18,23–28} We have previously described electrochemical stripping (ECS),^{29–32} a process that valorizes ammonium-rich wastewater through both electromigration and membrane stripping; we adapt and apply ECS to mediate Co(DIM)-catalyzed NO₃RR to NH₃, separate Co(DIM) from secondary effluent, and separate ammonia from secondary effluent. Our use of ECS in several configurations enables water treatment, facilitates catalyst reuse, and extracts a high-purity product, all of which influence the energy, economics, and scale of homogeneous molecular catalysis for wastewater nitrate treatment.

In this study, we use ECS as a reactive separation platform to demonstrate three novel contributions to overcoming wastewater-nitrate valorization barriers: (1) showing that the catalyst Co(DIM) can treat secondary effluent to the drinking water limit of 10 mg of NO₃-N/L and maintain >98% ammonia selectivity, (2) recovering generated ammonia as high-purity ammonium sulfate (a commodity fertilizer), and (3) establishing electrochemical engineering strategies that enhance nitrate removal rate, ammonia recovery rate, and energy consumption. These contributions illustrate broadly applicable mechanistic insights into process engineering of molecular electrocatalysis in wastewater valorization, electrified production of ammonia from nitrate emissions, and the design of reactive separation processes.

2. MATERIALS AND METHODS

All reagents were purchased from commercial vendors and used as received. Nanopure water (resistivity of 18.2 MΩ cm)

was used for all experiments and measurements unless stated otherwise.

2.1. CoDIM Synthesis. The perchlorate salt of $[\text{Co}(\text{DIM})\text{Br}_2]^+$ was prepared as detailed previously.³³ ^1H nuclear magnetic resonance spectra of $[\text{Co}(\text{DIM})\text{Br}_2]\text{ClO}_4$ [Varian Inova 600 at 600 MHz (Figure S1)] and ultraviolet-visible spectroscopy [UV-vis, Cary 60 UV-vis spectrophotometer (Figure S2)] confirmed the anticipated structure.

2.2. Electrochemical Methods. A BioLogic VSP or VMP-300 instrument was used to control the potential applied to the working electrode versus the reference electrode. All electrochemical experiments were recorded using 85% IR compensation based on the ohmic resistance obtained via high-frequency impedance testing.

2.2.1. Voltammetry. A three-electrode system in a beaker cell was employed. The working electrode was a 3 mm glassy carbon (GC) disk (BASi, MF-2012); the counter electrode was a 6 mm diameter graphite rod (BASi, MW-4131) in a glass chamber with a Teflon separator (BASi, MR-1196), and the reference electrode was a Ag/AgCl (3 M KCl) electrode (BASi, MF-2056). The 3 mm GC electrode was polished with 1 μm alumina slurry (BASi, MF-2054) in a figure-eight motion on a microcloth polishing pad (BASi, MF-1040) for 1 min. After being polished, the GC electrode was sonicated in nanopure water for 1 min and blown dry with N_2 .

2.2.2. Electrochemical Stripping. A three-chamber reactor was assembled with three square acrylic glass frames (122 mL volume, 8 cm $\times$ 8 cm $\times$ 1.9 cm) bolted together between two larger square acrylic glass plates (18 cm $\times$ 18 cm $\times$ 3 cm). For each chamber, 250 mL of electrolyte (or wastewater) was recirculated in batch at a rate of 61 mL/min. The anolyte, catholyte, and trap chamber solutions were 0.1 M KClO_4 , secondary effluent with 8 mM Co(DIM), and 0.1 M H_2SO_4 , respectively. A 10 cm $\times$ 10 cm piece of AISI 316 stainless steel mesh (37% open area, 0.25 mm wire diameter, Goodfellow Corp.) was exposed to the electrolyte as the working electrode, and Ti mesh coated with Ir mixed metal oxide (Magnet Special Anodes) was used as the counter electrode. A Ag/AgCl reference electrode (3 M KCl, BASi) was placed adjacent ($\sim$ 2 cm) to the cathode. The reactor was operated under a potentiostatic mode for 42 h. A potential of -1.05 V versus Ag/AgCl was applied to the working electrode using the reference electrode, and the full cell potential was measured by recording the working and counter electrode potentials. The anode and cathode chambers were separated by a cation exchange membrane (CMI-7000, Membranes International Inc.); the cathode and trap chambers were separated by a hydrophobic membrane (CLARCOR QP 952, CLARCOR Industrial Air).

2.2.3. Electrodialysis. A three-chamber reactor analogous to the ECS reactor was employed, but using an anion exchange membrane (AMI-7001, Membranes International Inc.) rather than a gas permeable membrane. A 4:3 volumetric mixture of real secondary effluent and RO brine [from secondary municipal effluent at a potable reuse facility (Section S1 of the Supporting Information)] was used as the feed solution to concentrate ammonium and nitrate within a similar order of magnitude.

3. RESULTS AND DISCUSSION

The mechanism for Co(DIM)-mediated NO_3RR to NH_3 involves a cascade of four catalytic turnovers in the reaction-diffusion layer, where active catalyst molecules perform

catalysis adjacent to the cathode surface (Figure 1a).³⁴ In each turnover, Co(DIM) is reduced at the cathode to produce a catalytically active complex that binds a reactant in the reaction-diffusion layer; the intermediate adduct [i.e., $\text{Q}-\text{NO}_3$ (Figure 1a)] reacts to generate the product and regenerate Co(DIM). Further details about the reaction mechanism can be found in previous studies.^{35–37}

We performed cyclic voltammetry (CV) in four electrolytes to identify the waveform and onset potential of Co(DIM)-mediated NO_3RR (Figure 1b). Cyclic voltammograms in 0.1 M KCl and 0.1 M KCl with 10 mM KNO_3 were nearly identical, suggesting that the glassy carbon cathode was inert toward NO_3RR . The cyclic voltammogram of Co(DIM) showed two quasi-reversible peaks in the potential range from 0.60 to -1.2 V versus Ag/AgCl, and addition of nitrate led to a catalytic reduction current with an onset potential of approximately -0.8 V versus Ag/AgCl.^{19,35} CV was then performed in secondary effluent (2.0 mM NO_3^- , full composition in Table S1) with and without Co(DIM) (Figure 1c). A catalytic current was observed in the presence of Co(DIM) with an onset potential of approximately -0.8 V versus Ag/AgCl, corresponding to Co(DIM)-mediated NO_3RR . By -1.2 V versus Ag/AgCl, an onset to HER was seen. Thus, we chose an operating potential of -1.05 V versus Ag/AgCl for subsequent experiments (negative of NO_3RR onset and positive of HER onset).

Figure 2 shows the electrochemical stripping with nitrate reduction (ECS- NO_3RR) recirculating batch process. The

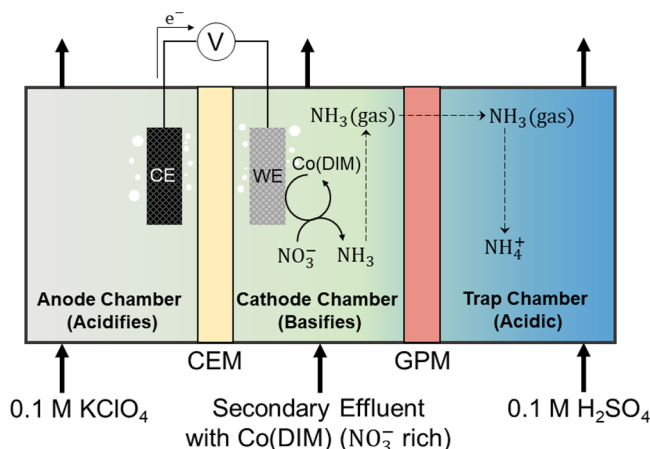


Figure 2. ECS- NO_3RR reactor. Electrolytes for each chamber are recirculated in batch to promote mixing and inform future continuous operation. A cation exchange membrane (CEM) separates the anode and cathode chamber, and a gas permeable membrane (GPM) separates the cathode and trap chamber. Co(DIM)-mediated NO_3RR in the cathode chamber produces an alkaline environment, allowing generated ammonia to diffuse across the GPM into the trap chamber. Ammonia in the trap chamber is protonated to ammonium, maintaining an ammonia concentration gradient between the cathode and trap chambers.

anode and cathode chamber are separated by a cation exchange membrane (CEM) to prevent diffusion of nitrate from the cathode chamber. The cathode chamber basifies to an alkaline pH [~ 10.3 (Figure S3)] from the reductive current. Because this pH is greater than the pK_a of ammonia (9.25), we expect $>90\%$ of TAN to exist as volatile ammonia. The cathode and trap chamber are separated by a hydrophobic gas

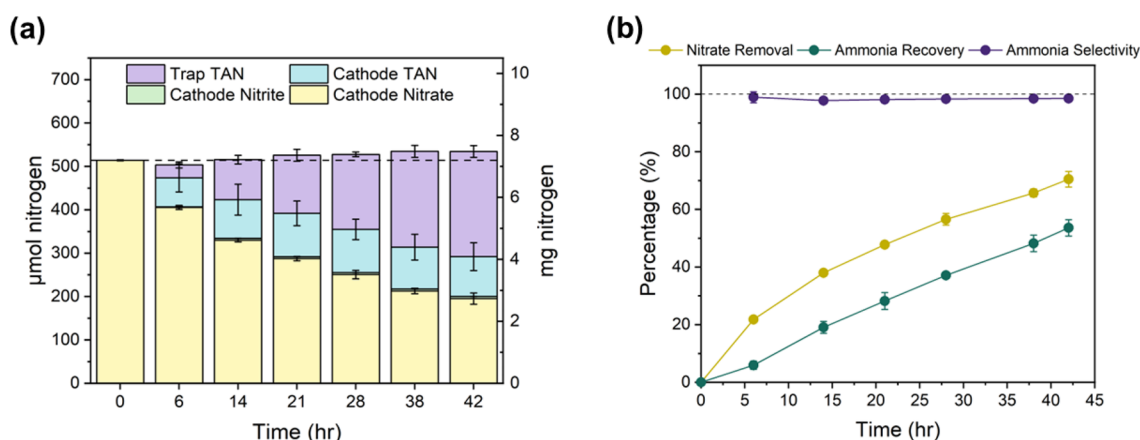


Figure 3. (a) Nitrogen mass balance for ECS-NO₃RR. Error bars represent $\pm$ one standard deviation from triplicate experiments ($n = 3$). (b) Nitrate removal (proportion of initial nitrate that has reacted), ammonia recovery (proportion of reacted nitrate recovered as ammonia in the trap chamber), and ammonia selectivity (proportion of reacted nitrate that is converted to ammonia) during ECS-NO₃RR. Equations for performance metrics are available in Section S2. Error bars represent $\pm$ one standard deviation ($n = 3$); error bars not shown are smaller than the symbol.

permeable membrane (GPM) to allow volatilized ammonia produced from NO₃RR to diffuse from the wastewater.

A nitrogen mass balance over the entire reactor is shown in Figure 3a. Nitrate was not detected in the anode and trap chambers, confirming membrane fidelity and lack of liquid transfer between chambers. TAN was not detected in the anode chamber, suggesting that its diffusion from the cathode chamber was exclusively through the GPM to the trap chamber. Nitrate and TAN close the entire nitrogen mass balance, underscoring the high product selectivity of Co(DIM) and the validity of using ion chromatography and flow injection analysis for species detection. A monotonic decrease in nitrate concentration was observed in the cathode chamber as Co(DIM)-mediated NO₃RR proceeded. Meanwhile, ammonia produced in the cathode chamber migrated to the trap, with no indication of other ions migrating to the trap (detection limits in Table S1). The slower rate of ammonia recovery versus nitrate removal (Figure 3b) reflects that migration of ammonia to the trap chamber is rate-limiting compared to Co(DIM)-mediated NO₃RR, in line with our previous studies of ECS.^{29,30} After operation for 42 h, $70.5 \pm 2.7\%$ nitrate removal was achieved, compared to 0% nitrate removal in the absence of Co(DIM). This removal corresponds to a final cathode chamber concentration of 9.25 mg of NO₃-N/L, which meets the drinking water limit of 10 mg of NO₃-N/L.³⁹ Ammonia selectivity never decreased below 98.5% throughout operation, demonstrating that the reaction selectivity of Co(DIM)-mediated NO₃RR was not affected by wastewater constituents. However, the effects of wastewater constituents on reaction activity and electrode fouling still need to be elucidated.

The electrical energy consumption of nitrate removal and ammonia recovery in ECS-NO₃RR was $\{0.34 \pm 0.03\}$ kWh/g of N (calculation in Section S2) for 2.0 mM NO₃[−], which is highly energy efficient compared to state-of-the-art electrocatalytic systems treating similar concentrations of nitrate [0.25–26.6 kWh/g of N for 0.3–3.6 mM NO₃[−] (Table S2)]. The energy consumption of conventional nitrogen management, HB process for ammonia production and nitrification-denitrification (NDN) for nitrate removal, is roughly 0.017 kWh/g of N (Section S4). Closing the ~ 20 -fold difference in energy consumption between ECS-NO₃RR and conventional nitrogen management (NDN and HB) is an achievable goal

that can be pursued through multiple avenues. For example, catalyst design (e.g., introducing new functional groups on the ligand and employing different metal centers) could decrease electrical energy consumption by increasing the Faradaic efficiency of NH₃ production [10–15% in ECS-NO₃RR (Figure S4)], decreasing the overpotential of the reaction, and accelerating the intrinsic reaction kinetics.³⁸ We consider catalyst design to be out of the scope of this work and instead focus on ECS-NO₃RR and its flexibility as a platform to recover TAN from both nitrate- and ammonium-rich wastewaters. We explored two additional process configurations that improve electrical energy consumption, ammonia recovery rate, and nitrate removal rate. In a parallel feed configuration (Figures S5 and S6), ammonium-rich reverse osmosis (RO) brine [16.2 mM NH₄⁺ (composition in Table S1)] is fed to the anode chamber in parallel with the secondary effluent being fed to the cathode chamber. The rate of removal of nitrate from the secondary effluent was unaffected; the rate of recovery of ammonia was enhanced by 17-fold, and electrical energy consumption was halved to 0.17 kWh/g of N. In a second configuration, we intensify the parallel feed process by concentrating nitrate and ammonium (to 17.3 mM NO₃[−] and 101.9 mM NH₄⁺, respectively) from a mixture of secondary effluent and RO brine in an electrodialysis (ED) cell (Figures S7 and S8). In this ED-concentrated parallel configuration, Co(DIM) is added to the concentrated nitrate solution rather than to the wastewater, avoiding the need for separating the catalyst from wastewater. The concentrated feedstocks are fed to the ECS-NO₃RR reactor, providing greater driving force for reaction and separation. The rates of removal of nitrate and recovery of ammonia increased by ~ 10 - and 95-fold, respectively, compared to those of the ECS-NO₃RR experiments depicted in Figure 3, with an ECS-NO₃RR energy consumption of 0.13 kWh/g of N. Table S3 and Figures S9–S12 summarize performance among the process configurations, while Table S4 shows performance comparisons with state-of-the-art electrochemical technologies. The additional ECS-NO₃RR process configurations provide preliminary examples of how process optimization efforts can be approached and how the process can be tuned to treat multiple reactive nitrogen pollutants.

In this study, we demonstrated separation of the product from the treated wastewater and homogeneous catalyst. To

extend this work, separation of the catalyst from treated wastewater would enable catalyst reuse and downstream wastewater treatment. The charge and molecular weight of Co(DIM) make ion exchange and membrane filtration viable options for separation of the catalyst from the treated secondary effluent,^{40,41} which could be integrated with electrolyzer-based approaches like ECS-NO₃RR.^{31,42} We also highlight that the ED-concentrated parallel configuration (Figure S7) could enable reuse of the dissolved catalyst by reintroducing nitrate from fresh wastewater feed.

This work addresses three key challenges at the intersection of the molecular catalysis field and water treatment. First, we demonstrate that wastewaters (secondary effluent and RO brine) do not preclude molecular catalysts from functioning with high product selectivities (>98.5%). Second, we recover the generated ammonia as high-purity ammonium sulfate, a commodity fertilizer. Lastly, we showcase unit process configurations of ECS-NO₃RR that enable separation of the catalyst from wastewater. ECS-NO₃RR lends control at the unit process level for reaction and separation steps and exhibits an energy consumption within an order of magnitude of the state-of-the-art process (HB and NDN). The electrochemical engineering approaches presented in this study may be generalizable to other molecular catalysts and wastewaters and encourage further investigations into molecular electrocatalysis for wastewater treatment, resource recovery, and reactive separation processes.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.estlett.3c00205>.

Details about the calculation of performance metrics, wastewater composition, catalyst characterization, additional reactor configurations, and a discussion of energy and performance (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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