Supplementary Information for:

Engineering a molecular electrocatalytic system for energy-efficient ammonia production
from wastewater nitrate

Dean M. Miller¹, Matthew J. Liu¹, Kristen Abels¹, Anna Kogler², Kindle S. Williams,¹ William A.
Tarpeh¹,²,³,*

¹Department of Chemical Engineering, Stanford University, Stanford, CA, 94305, United States
²Department of Civil and Environmental Engineering, Stanford University, Stanford, CA, 94305, United States
³Woods Institute for the Environment, Stanford University, Stanford, California 94305, United States

*Corresponding author, Email: wtarpeh@stanford.edu. Address: 443 Via Ortega, Room 387, Stanford CA, 94305, USA. Telephone: (650) 497-1324

65 pages
7 tables
39 figures
44 equations

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Fig. S1. $^1$H NMR of Co(DIM) in CD$_3$OD (deuterated methanol).
Fig. S2. Mass spectra for aqueous Co(DIM). Co(DIM) samples were prepared for high performance liquid chromatography-mass spectrometry (HPLC-MS) analysis by diluting 1 mg/mL aqueous solutions by a factor of 5 using a methanol/water mixture (50:50 v/v). Samples were analyzed via direct injection on an Agilent 1260 HPLC with an Agilent 6460 Triple Quadrupole MS (Agilent, Santa Clara, CA). Samples were eluted using 98% aqueous mobile phase (0.1% formic acid) and 2% organic mobile phase (acetonitrile) at a flowrate of 0.6 mL/min. 10 μL of sample were injected during each run. Compounds were detected using positive electrospray ionization mode with a gas temperature of 300 ºC, gas flowrate of 7 L/min, a nebulizer pressure of 45 psi, a sheath gas temperature of 250 ºC, a sheath gas flowrate of 9 L/min, a capillary voltage of 3500 V, a nozzle voltage of 500 V, a fragmentor energy of 50 V, and a cell accelerator voltage of 7 V.
LC-MS fragment weights match reasonably well with the molecular weight of Co(DIM) bound to zero
Br⁻ ions (283.29), one Br⁻ ion (363.19), and two Br⁻ ions (443.09). Additionally, ⁷⁹Br and ⁸¹Br exist in
roughly equal parts naturally at standard temperature and pressure, causing the spectra to exhibit a triplet
at 442.8 m/z, a doublet at 361.9 m/z, and a singlet at 280.9 m/z.
Fig. S3. Photos of electrocatalyst-in-a-box (ECaB) reactor. Top photo: ECaB reactor profile before being plumbed with recirculation tubing. Bottom left photo: three-chamber extraction/recovery cell (bottom), two-chamber electrocatalysis reactor (top). Bottom right photo: flow setup showing reactor system, pumps, and batch recirculation bottles.
Table S1. Simplified, simulated, and real wastewater characterization.

<table>
<thead>
<tr>
<th>Species*</th>
<th>Simplified Wastewater</th>
<th>Simulated Wastewater</th>
<th>Real Wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>28 mg-N/L</td>
<td>28 mg-N/L</td>
<td>28 mg-N/L</td>
</tr>
<tr>
<td>Chloride</td>
<td>217 mg/L</td>
<td>242 mg/L</td>
<td>228 mg/L</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>-</td>
<td>84 mg/L</td>
<td>79 mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>-</td>
<td>106 mg/L</td>
<td>102 mg/L</td>
</tr>
<tr>
<td>Sodium</td>
<td>52.2 mg/L</td>
<td>120 mg/L</td>
<td>120 mg/L</td>
</tr>
<tr>
<td>Potassium</td>
<td>20 mg/L</td>
<td>20 mg/L</td>
<td>20 mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>36 mg/L</td>
<td>36 mg/L</td>
<td>36 mg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>76 mg/L</td>
<td>77 mg/L</td>
<td></td>
</tr>
<tr>
<td>pH (without 8 mM Co(DIM))</td>
<td>6.50</td>
<td>8.55</td>
<td>8.30</td>
</tr>
<tr>
<td>pH (with 8 mM Co(DIM))</td>
<td>3.06</td>
<td>3.42</td>
<td>3.58</td>
</tr>
</tbody>
</table>

*Fluoride, nitrite, bromide, phosphate, and lithium were measures but not detected in the real wastewater by ion chromatography.
Section S2: Cyclic voltammetry (CV)

Fig. S4. a) CVs as a function of [Co(DIM)] in the absence of nitrate. b) CVs as a function of Co(DIM) with 2 mM nitrate (2 mM NaNO$_3$). Working electrode: 5 mm GC disk. Counter electrode: 6.6 mm graphite rod. Reference electrode: Ag/AgCl (4.0 M KCl). Background electrolyte: 6.2 mM NaCl.
Fig. S5. CVs of 8 mM Co(DIM) in real secondary effluent wastewater and in simplified wastewater (6.2 mM NaCl + 2 mM NaNO₃) for comparison. Working electrode: 5 mm GC disk. Counter electrode: 6.6 mm graphite rod. Reference electrode: Ag/AgCl (4.0 M KCl).
Section S3: Controlled-potential electrolysis (CPE)

Section S3.1: Equations used to evaluate CPEs

\[ S_{\text{TAN}} = \frac{\text{mol} \ TAN_{\text{produced}}}{\text{mol} \ NO_3^{\text{(initial)}} - \text{mol} \ NO_3^{\text{(t)}}} \]  

(Equation S3.1.1)

\[ FE \ t o \ TAN \ (\%) = \left( \frac{n \times F \times \text{mol} \ TAN_{\text{produced}}}{Q_{\text{passed}}} \right) \times 100\% \]  

(Equation S3.1.2)

where

\[ n \] = number of electrons (8) required to produce one mole of TAN from NO\textsubscript{3}\textsuperscript{−}, Q\textsubscript{passed} = charge passed in units of C

and \( F = 96485 \ C \ mol^{-1} \)

\[ X_{\text{NO}_3^{-}}(t) = \frac{\text{mol} \ NO_3^{\text{(initial)}} - \text{mol} \ NO_3^{\text{(t)}}}{\text{mol} \ NO_3^{\text{(initial)}}} \]  

(Equation S3.1.3)
Section S3.2: Aqueous characterization of CPE experiments

Fig. S6. Cation chromatograms of aqueous samples from CPEs in modified simplified wastewater (8 mM Co(DIM) + 6.2 mM NaCl) and in simplified wastewater (8 mM Co(DIM) + 6.2 mM NaCl + 2 mM NaNO₃).
Fig. S7. Charge decomposition into the first Co(DIM) reduction, second Co(DIM) reductions, and NO$_3$RR.

-1.05 V vs. Ag/AgCl applied for NO$_3$RR (yellow; simplified wastewater: 8 mM Co(DIM) + 6.2 mM NaCl + 2 mM NaNO$_3$) and 2$^{\text{nd}}$ Co(DIM) reduction (green; modified simplified wastewater: 8 mM Co(DIM) + 6.2 mM NaCl). –0.75V vs. Ag/AgCl (–0.99 V vs. first reduction, +0.25 V vs. second reduction) applied for 1$^{\text{st}}$ Co(DIM) reduction (purple; simplified wastewater: 8 mM Co(DIM) + 6.2 mM NaCl + 2 mM NaNO$_3$).

Error bars represent ± one standard deviation from triplicate experiments (n=3) for NO$_3$RR experiments (yellow; simplified wastewater: 8 mM Co(DIM) + 6.2 mM NaCl + 2 mM NaNO$_3$). The CPE experiments to quantify charge associated with non-catalytic 1$^{\text{st}}$ and 2$^{\text{nd}}$ reductions of Co(DIM) were only performed once because no conversion of nitrate and no production of TAN was observed.
Section S3.3: Post CPE characterization

Fig. S8. Photos of GC cathodes post CPE in (a) simplified, (b) simulated, and (c) real wastewater. −1.05 V vs. Ag/AgCl was held for 8 hours, then the cathode was removed, rinsed thoroughly with water, and blown dry with N₂. The anode was a 5.4 cm² MMO electrode. Leakless Ag/AgCl (3.4 M KCl) reference electrode. Cathode and anode chambers were separated by a CEM.
Table S2. Possible precipitates from real secondary effluent wastewater.

<table>
<thead>
<tr>
<th>Possible precipitate</th>
<th>Concentration of relevant ions in real wastewater</th>
<th>$K_{sp}$ of precipitate$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)$_2$</td>
<td>$[\text{Mg}^{2+}] = 1.5 \text{ mM}$</td>
<td>$5.61 \times 10^{-12}$</td>
</tr>
<tr>
<td></td>
<td>$[\text{OH}^-]<em>{\text{RDL}} = 10^{-(14 - \text{pH}</em>{\text{RDL}})}$</td>
<td></td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td>$[\text{Mg}^{2+}] = 1.5 \text{ mM}$</td>
<td>$6.82 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$[\text{HCO}_3^-] = 1.4 \text{ mM}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$[\text{CO}_3^{2-}] = 1.4 \text{ mM}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\left[\text{HCO}<em>3^-\right] = 10^{-pK</em>{a\text{HCO}_3/CO}_3^{2-}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\left[\text{CO}<em>3^{2-}\right]</em>{\text{RDL}} = 10^{-pK_{a\text{HCO}_3/CO}_3^{2-}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$pK_{a\text{HCO}_3/CO}_3^{2-} = 10.3$</td>
<td></td>
</tr>
<tr>
<td>MgSO$_4 \cdot 7\text{H}_2\text{O}$</td>
<td>$[\text{Mg}^{2+}] = 1.5 \text{ mM}$</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
<td>$[\text{SO}_4^{2-}] = 1.1 \text{ mM}$</td>
<td>$(\text{soluble in water up to 1.1 kg/L})$</td>
</tr>
<tr>
<td>Ca(OH)$_2$</td>
<td>$[\text{Ca}^{2+}] = 1.9 \text{ mM}$</td>
<td>$5.02 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$[\text{OH}^-]<em>{\text{RDL}} = 10^{-(14 - \text{pH}</em>{\text{RDL}})}$</td>
<td></td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>$[\text{Ca}^{2+}] = 1.9 \text{ mM}$</td>
<td>$3.36 \times 10^{-9}$*</td>
</tr>
<tr>
<td></td>
<td>$[\text{HCO}_3^-] = 1.4 \text{ mM}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\left[\text{HCO}<em>3^-\right] = 10^{-pK</em>{a\text{HCO}_3/CO}_3^{2-}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\left[\text{CO}<em>3^{2-}\right]</em>{\text{RDL}} = 10^{-pK_{a\text{HCO}_3/CO}_3^{2-}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$pK_{a\text{HCO}_3/CO}_3^{2-} = 10.3$</td>
<td></td>
</tr>
<tr>
<td>CaSO$_4 \cdot 2\text{H}_2\text{O}$</td>
<td>$[\text{Mg}^{2+}] = 1.5 \text{ mM}$</td>
<td>$3.14 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
\[
\text{SO}_4^{2-} = 1.1 \text{ mM}
\]

\(K_{sp}\) shown for CaCO\(_3\) corresponds to calcite, which has the lowest \(K_{sp}\) among possible precipitates.

To determine the interfacial pH required for precipitation of Mg(OH\(_2\)) we began by setting the solubility product quotient \((Q_{sp})\) equal to the solubility product constant \((K_{sp})\).

\[
Q_{sp} = [Mg^{2+}][OH^-]^2 = K_{sp} = 5.61 \times 10^{-12}
\]

(Equation S3.3.1)

Plugging in \([Mg^{2+}] = 1.5 \text{ mM}\) and solving for \([OH^-]\) yields the pH necessary for precipitation of Mg(OH\(_2\)) in the RDL: pH\(_{RDL}\) = 9.8. The same procedure was used to determine the necessary pH for precipitation of Ca(OH)\(_2\): pH\(_{RDL}\) = 12.8.

Determining the interfacial pH required for precipitation of carbonates like MgCO\(_3\) is only slightly more complex because of the \(HCO_3^-/CO_3^{2-}\) acid/base pair, where magnesium and calcium bicarbonate are significantly more soluble than their carbonate analogues. We again set \(Q_{sp}\) equal to \(K_{sp}\).

\[
Q_{sp} = [Mg^{2+}][CO_3^{2-}] = K_{sp} = 6.82 \times 10^{-6}
\]

(Equation S3.3.2)

Plugging in \([Mg^{2+}] = 1.5 \text{ mM}\) and solving for \([CO_3^{2-}]\) yields the \([CO_3^{2-}]\) necessary for precipitation of MgCO\(_3\) in the RDL: 4.5 mM. This concentration is greater than the 1.4 mM bicarbonate in bulk solution, making precipitation of MgCO\(_3\) unlikely. We performed the same procedure for CaCO\(_3\).

\[
Q_{sp} = [Ca^{2+}][CO_3^{2-}] = K_{sp} = 3.36 \times 10^{-9}
\]

(Equation S3.3.3)

Precipitation of CaCO\(_3\) is possible because the \([CO_3^{2-}]\) necessary is 1.8 \(\mu\)M. Because the bulk pH of the Real Wastewater was 8.30 << \(pK_a^{HCO_3^-/CO_3^{2-}} = 10.3\), the majority of inorganic carbon in bulk solution exists as bicarbonate. The concentration of carbonate is therefore dependent on the RDL pH assuming the acid/base pair is equilibrated by rapid proton transfer kinetics.

\[
10^{-pK_a^{HCO_3^-/CO_3^{2-}}} \times 10^{-pH_{RDL}} = \frac{[CO_3^{2-}]_{RDL}}{[HCO_3^-]_{RDL}}
\]

(Equation S3.3.4)
\[ 10^{-pH_{RD\text{L}}} = \frac{10^{-pK_a}_{HCO_3^-/CO_3^{2-}} \times [HCO_3^-]_{RD\text{L}}}{[CO_3^{2-}]_{RD\text{L}}} \]  
(Equation S3.3.5)

\[ pH_{RD\text{L}} = -\log \left( \frac{10^{-pK_a}_{HCO_3^-/CO_3^{2-}} \times [HCO_3^-]_{RD\text{L}}}{[CO_3^{2-}]_{RD\text{L}}} \right) \]  
(Equation S3.3.6)

The unknown \([HCO_3^-]_{RD\text{L}}\) can be eliminated by a mass balance of bicarbonate and carbonate.

\[ pH_{RD\text{L}} = -\log \left( \frac{10^{-pK_a}_{HCO_3^-/CO_3^{2-}} \times (1.4 \text{ mM} - [CO_3^{2-}]_{RD\text{L}})}{[CO_3^{2-}]_{RD\text{L}}} \right) \]  
(Equation S3.3.7)

Plugging in \([CO_3^{2-}]_{RD\text{L}} = 1.8 \mu\text{M}\), the RDL pH necessary for precipitation of CaCO\(_3\) is 4.4 which is less than the pH of the bulk solution. Complex aqueous solutions like the real wastewater in this study are nevertheless able to keep Ca\(^{2+}\) and HCO\(_3^-\) solvated in bulk solution. We hypothesize that interfacial coulombic effects in Co(DIM)-mediated NO\(_3\)RR prevented CaCO\(_3\) deposition and may explain why we did not see a strong signal for calcium in XPS or EDS for any GC cathode analyzed. One such effect could be Co(DIM) axially coordinating bicarbonate/carbonate,\(^3\) precluding deposition.

Finally, precipitation of magnesium as a sulfate is unlikely because the hydrate (MgSO\(_4\) \(\cdot\) 7H\(_2\)O) is soluble in mass fractions greater than 1:1 with water. Precipitation of CaSO\(_4\) \(\cdot\) 2H\(_2\)O is also unlikely because the concentration of sulfate necessary (16.5 mM) exceeds the concentration in the real wastewater (1.1 mM), as shown by setting \(Q_{sp}\) equal to \(K_{sp}\) in Equation S3.3.8.

\[ Q_{sp} = [Ca^{2+}] [SO_4^{2-}] = K_{sp} = 3.14 \times 10^{-5} \]  
(Equation S3.3.8)
Fig. S9. pH trends of 2-chamber CPEs as a function of time. Error bars represent ± one standard deviation from triplicate experiments (n=3). Error bars not shown are smaller than the symbol.
Fig. S10. EDS spectra of GC cathode post CPE in real wastewater.
Fig. S11. EDS dark field maps of C, Ca, Co, Mg, N, O, P, and Si on GC electrodes post real wastewater CPE.
Fig. S12. Nitrogen mass balances for the rinse test (in simplified wastewater) of the deposit formed in {8 mM Co(DIM) + simplified wastewater}. No TAN or $\text{NO}_2^-$ was detected by ion chromatography. Detection limit for $\text{NO}_2^-$: 0.25 mg/L. Detection limit for TAN: 0.25 mg/L.
Fig. S13. N mass balances for the rinse test (in simplified wastewater) of the deposit formed in {8 mM Co(DIM) + real wastewater}. No TAN or NO$_2$ was detected by ion chromatography. Detection limit for NO$_2$: 1.0 mg/L. Detection limit for TAN: 0.25 mg/L.
Fig. S14. a) Nyquist plots for potentiostatic electrochemical impedance spectroscopy (PEIS) of deposits formed in CPE. The electrolyte was 8 mM Co(DIM) + 6.2 mM NaCl + 2 mM NaNO₃ and the measurement was performed at open circuit with a sinusoidal potential amplitude of 10 mV and a frequency range of 1 MHz to 10 mHz. An electrochemical cone cell was used with a circular working electrode opening 5 mm in diameter. The counter electrode was a 6.4 mm graphite rod and the reference electrode was a Ag/AgCl (4.0 M KCl) electrode. $R_{ct}$ was calculated by fitting a semi-circle to the region of the Nyquist plot before the Warburg, then subtracting $R_u$ (the low x-intercept of the Nyquist plot) from $R_{ct} + R_u$ (the high x-intercept).₄₅ b) Measured $R_{ct}$ values from PEIS.
Section S4: Transport and contaminant conditions for catalysis inhibition

Section S4.1: Rotating disk electrode

To interrogate the sensitivity of inhibition to interfacial electrolyte composition, we used a rotating-disk electrode (RDE) to achieve well-defined transport conditions in the RDL. By varying the rotation rate, we modulated the delivery rate (and therefore steady-state concentrations) of \( \text{NO}_3^- \), Co(DIM), and wastewater constituents during CPE. Under stagnant conditions (0 rotations per minute (RPM)), the current density of Co(DIM)-mediated NO\(_3\)RR in simplified wastewater (2 mM \( \text{NO}_3^- \)) was greater than that of Co(DIM) in simplified wastewater (0 mM \( \text{NO}_3^- \)), demonstrating steady-state catalytic current (Fig. 3a).

Catalytic current in simplified wastewater was also observed with rotation rates of 9 and 25 RPM, indicating that homogeneous NO\(_3\)RR outpaces bulk catalyst delivery to the electrode surface with modest forced convection.\(^6\) Conversely, catalytic current is lost in the range of 100 to 400 RPM, indicating that bulk catalyst delivery outpaces NO\(_3\)RR (Fig. S15). The rotation rates tested therefore span transport conditions for Co(DIM)-mediated NO\(_3\)RR catalysis and for Co(DIM) activation with no catalysis. In real wastewater (2 mM \( \text{NO}_3^- \)), the current density vs. time effectively overlays with the simplified wastewater (2 mM \( \text{NO}_3^- \)) for the duration of the 5 min CPE, indicating no inhibition under stagnant conditions. Disturbing the RDL by forced convection causes a decay in current density in real wastewater, indicating inhibition. The coupled transport conditions and bulk solution composition for a fixed electrode potential therefore describe inhibition conditions.
Fig. S15. (a) Current density vs. time for controlled-potential electrolysis (CPE) at –1.05 V vs. Ag/AgCl performed in a rotating-disk electrode (RDE) setup with 8 mM Co(DIM) as a function of rotations per minute (RPM) in three electrolyte: simplified wastewater (0 mM NO₃⁻), simplified wastewater (2 mM NO₃⁻), and real wastewater (2 mM NO₃⁻). The controlled rotation rate varied the delivery of NO₃⁻, Co(DIM), and wastewater constituents to the RDL while the current density was monitored as a proxy for the NO₃RR activity. Rotation rates were kept below 400 RPM because faster rotation rates resulted in loss of catalytic current (i.e., the same current density was observed for simplified wastewater (0 mM NO₃⁻) and simplified wastewater (2 mM NO₃⁻)). b) Steady-state currents of RDE CPEs from Fig. 3a plotted versus the square root of rotation rate (a proxy for diffusion layer thickness⁵). In the presence of nitrate and under sufficiently fast rotation rates, bulk catalyst delivery outpaces NO₃RR, causing the green and blue points to be nonlinear.
Fig. S16. Chronoamperogram for longer Mg dose RDE CPE experiment. $-1.05 \text{ V}_{\text{Ag/AgCl}}$ was applied from $t = 0$ to 50 minutes. 28 $\mu$L of 1 M MgCl$_2$ was injected into the electrolyte at $t = 10$ min. Then a period of open circuit potential (OCP) was held from $t = 50$ min to 60 min. Finally, $-1.05 \text{ V}_{\text{Ag/AgCl}}$ was applied from $t = 60$ to 110 minutes.
Section S4.2: Two-chamber CPE contaminant dosing experiments

In contaminant dosing experiments, the same two-chamber CPE setup was used as described in Materials & Methods 2.2.2. After the 2 h sample aliquots were drawn from cathode and anode chambers, a small volume of 1 M salts were manually injected (70 μL 1 M MgCl₂, 75 μL 1 M NaHCO₃, 95 μL 1 M CaCl₂) into the catholyte recirculation bottle. The volume was chosen such that the catholyte concentration of the target contaminant matched the target contaminant concentration in real wastewater.

Fig. S17. N mass balance for two-chamber CPE experiment. 95 μL 1 M CaCl₂ injected into the catholyte at t = 2 h.
Fig. S18. N mass balance for $\text{Mg}^{2+}$ dose two-chamber CPE experiment. 70 $\mu$L 1 M MgCl$_2$ injected into the catholyte at $t = 2$ h.
Fig. S19. N mass balance for \( \text{HCO}_3^- \) dose two-chamber CPE experiment. 75 μL 1 M NaHCO\(_3\) injected into the catholyte at \( t = 2 \) h.
Fig. S20. N mass balance for simultaneous and dose CPE experiment. 75 μL 1 M NaHCO$_3$ and 70 μL 1 M MgCl$_2$ injected into the catholyte at t = 2 h.
Fig. S21. Nitrate conversion for contaminant dose two-chamber CPE experiments.
Fig. S22. Mg mass as a function of time for real wastewater CPE, simulated wastewater CPE, and Mg dose CPE. Error bars represent ± one standard deviation from triplicate experiments (n=3). Note that Mg dose CPE data are from one experiment. Consumption of Mg in real wastewater CPE: 8.6 ± 1.3%. Consumption of Mg in Simulated wastewater CPE: 15.3 ± 1.3%. Consumption of Mg in Mg dose CPE: 10.6%.
Section S5: Electrocatalyst-in-a-box (ECaB)

Section S5.1: Equations used to evaluate ECaB

Efficiencies

\[ \eta_{\text{NO}_3 \text{ extraction}} = \frac{\text{mol NO}_3^- \text{wastewater (initial)} - \text{mol NO}_3^- \text{wastewater (t)}}{\text{mol NO}_3^- \text{wastewater (initial)}} = \frac{\text{mol NO}_3^- \text{extracted (t)}}{\text{mol NO}_3^- \text{wastewater (initial)}} \]  
(Equation S5.1.1)

\[ X_{\text{NO}_3} = \frac{\text{mol NO}_3^- \text{converted (0 h CPE)} - \text{mol NO}_3^- \text{extracted (t)}}{\text{mol NO}_3^- \text{extracted (t)}} = \frac{\text{mol NO}_3^- \text{converted (t)}}{\text{mol NO}_3^- \text{extracted (t)}} \]  
(Equation S5.1.2)

\[ Y_{\text{TAN}} = X_{\text{NO}_3} \ast S_{\text{TAN}} = \frac{\text{mol TAN produced (t)}}{\text{mol NO}_3^- \text{extracted (t)}} \]

where for ECaB, \( \text{mol TAN produced (t)} = \text{mol TAN catholyte (t)} + \text{mol TAN trap (t)} \)  
(Equation S5.1.3)

\[ \eta_{\text{TAN, recovery}} = \frac{\text{mol TAN trap (t)}}{\text{mol TAN produced (t)}} = \frac{\text{mol TAN recovered (t)}}{\text{mol TAN produced (t)}} \]  
(Equation S5.1.4)

\[ \eta_{\text{N recovery, overall}} = \frac{\text{mol TAN recovered (t)}}{\text{mol NO}_3^- \text{wastewater (initial)}} \]  
(Equation S5.1.5)*

\[ \eta_{\text{N recovery, overall}} = \eta_{\text{NO}_3 \text{ extraction}} \ast Y_{\text{TAN}} \ast \eta_{\text{TAN, recovery}} = \frac{\text{mol TAN trap (t)}}{\text{mol NO}_3^- \text{wastewater (initial)}} \]  
(Equation S5.1.6)*
η\textsubscript{overall} was calculated by Equations S5 and S6 and both datasets are shown in Fig. SX. Data calculated by Equations S5 and S6 are in agreement within experimental error for all time points.

$$FE \text{ to } TAN \left(\%\right) = \left(\frac{n \ast F \ast mol \ TAN_{produced}}{Q_{passed}}\right) \ast 100\%$$

(Equation S5.1.7)

where \( n \) = number of electrons (8) required to produce one mole of TAN from NO\textsubscript{3}⁻, \( Q_{passed} \) = charge passed in CPE in units of C, and \( F \) = 96485 C mol\(^{-1}\).

**Rates**

\(Areal\ \text{NO}_3^-\ \text{extraction rate} = \frac{mol \ \text{NO}_3^-_{ex} (t)}{t \ast A_{cross \ sectional}}\)

(Equation S5.1.8)

\(Volumetric\ \text{NO}_3^-\ \text{extraction rate} = \frac{mol \ \text{NO}_3^-_{ex} (t)}{t \ast V_{wastewater}}\)

(Equation S5.1.9)

\(Areal\ \text{NO}_3^-\ \text{conversion rate} = \frac{mol \ \text{NO}_3^-_{cn} (t_{CPE})}{t_{CPE} \ast A_{cross \ sectional}}\)

(Equation S5.1.10)

\(Volumetric\ \text{NO}_3^-\ \text{conversion rate} = \frac{mol \ \text{NO}_3^-_{cn} (t_{CPE})}{t_{CPE} \ast V_{catholyte}}\)

(Equation S5.1.11)

\(Areal\ \text{TAN} \ \text{production (yield) rate} = \frac{mol \ TAN_{produced} (t_{CPE})}{t_{CPE} \ast A_{cross \ sectional}}\)

(Equation S5.1.12)

\(Volumetric\ \text{TAN} \ \text{production (yield) rate} = \frac{mol \ TAN_{produced} (t_{CPE})}{t_{CPE} \ast V_{catholyte}}\)

(Equation S5.1.13)

\(Areal\ \text{TAN} \ \text{recovery rate} = \frac{mol \ TAN_{recovered} (t)}{t \ast A_{cross \ sectional}}\)

(Equation S5.1.14)

\(Volumetric\ \text{TAN} \ \text{recovery rate} = \frac{mol \ TAN_{recovered} (t)}{t \ast V_{catholyte}}\)

(Equation S5.1.15)

\(Psuedo\ \text{instant.} \ [\text{NO}_3^-] \ \text{normalized conversion rate} = \frac{mol \ \text{NO}_3^-_{cn} (t) - mol \ \text{NO}_3^-_{cn} (t - 1)}{C_{\text{NO}_3^-_{catholyte}} (t - 1) \ast V_{catholyte}}\)

(Equation S5.1.16)
Energy consumption

Energy consumed for NO$_3^-$ extraction = \( \frac{E_{\text{cell,av}} \times Q_{\text{passed}}}{\text{mol NO}_3^- \text{extracted}(t)} \) (Equation S5.1.17)

Energy consumed for NO$_3^-$ conversion = \( \frac{E_{\text{cell,av}} \times Q_{\text{passed}}}{\text{mol NO}_3^- \text{converted}(t)} \) (Equation S5.1.18)

Energy consumed for TAN production = \( \frac{E_{\text{cell,av}} \times Q_{\text{passed}}}{\text{mol TAN}_\text{produced}(t)} \) (Equation S5.1.19)

Energy consumed for TAN recovery = \( \frac{E_{\text{cell,av}} \times Q_{\text{passed}}}{\text{mol TAN}_\text{recovered}(t)} \) (Equation S5.1.20)

Electricity operational expenditure

Recovered (NH$_4$)$_2$SO$_4$ cost = \( \frac{E_{\text{cell,av}} \times Q_{\text{passed}}}{\text{mol TAN}_\text{recovered}(t)} \times \$3 \) kWh

(Equation S5.1.21)

Equation 5.1.21 was used to calculate the cost of producing purified ammonium sulfate when considering electricity as the only operational expenditure at a cost of \$3 \text{ kWh}^{-1}.\)
Section S5.2: Proof-of-concept ECaB pH, rates, efficiencies, and cathode characterization

Fig. S23. pH trends of the 4 chambers in proof-of-concept ECaB. Error bars represent ± one standard deviation from triplicate experiments (n=3).
Fig. S24. Binding of TAN to Co(DIM). Experiments were carried out by adding 0, 1, 2, 4, 8, 16, or 32 mM NH₃ (as NH₄OH) to vials of 1 M KCl + 8 mM Co(DIM), pH 10.5. Vials were shaken vigorously for 4 h, acidified with concentrated H₂SO₄, and then TAN was measured by cation IC. (a) TAN concentration detected by cation IC as a function of NH₃ concentration added. Deviation from the dotted line (y = x) indicates TAN adsorption by Co(DIM). (b) Percent of TAN detected as a function of NH₃ added. More of the added nitrogen binds to Co(DIM) at low NH₃ concentrations. (c) Observed TAN binding capacity of Co(DIM).
Fig. S25. Concentration of Co ($^{60}$Co) in each chamber of proof-of-concept ECaB at initial (0 h) and final (96 h) time points. Co concentration was below detection (0.85 μM) for the initial and final wastewater time points, and for the initial trap and anode time points. These data demonstrate that Co(DIM) remained in the cathode chamber of ECaB proof-of-concept. Error bars represent ± one standard deviation from triplicate experiments (n=3).
Fig. S26. Overall N recovery of proof-of-concept ECaB calculated two ways. Black trace was calculated as the mass of TAN in the trap divided by the initial mass of nitrate-nitrogen in the wastewater (Equation S5.1.5). Blue was calculated by multiplying the nitrate extraction efficiency, the yield of TAN, and the TAN recovery efficiency (Equation S5.1.6). Error bars represent ± one standard deviation from triplicate experiments (n=3).
Fig. S27. Amount (in milliequivalents of charge) of nitrate and sulfate ions in wastewater chamber as a function of time for proof-of-concept ECaB. Error bars represent ± one standard deviation from triplicate experiments (n=3).
Fig. S28. Extraction flux (normalized to concentration in milliequivalents of charge) of nitrate and sulfate ions as a function of time for proof-of-concept ECaB. Error bars represent ± one standard deviation from triplicate experiments (n=3).
Fig. S29. Extraction selectivity (calculated as the fraction of nitrate flux divided by sulfate flux) of nitrate ions over sulfate ions as a function of time for proof-of-concept ECaB. Error bars represent ± one standard deviation from triplicate experiments (n=3).
Fig. S30. XPS Mg 1s scans at three locations of one glassy carbon cathode after proof-of-concept ECaB experiment.
Fig. S31. EDS spectrum of glassy carbon cathode after proof-of-concept ECaB experiment. A small amount of Cu was found on the surface, presumably the from Cu tape used as electrical leads to the GC plate cathode and mixed-metal oxide anode.
Fig. S32. a) Areal (normalized to AEM area) and b) volumetric (normalized to wastewater volume) nitrate extraction rates. c) Areal (normalized to GC area) and d) volumetric (normalized to catholyte volume) nitrate conversion rates. e) Areal (normalized to GC area) and f) volumetric (normalized to catholyte volume) TAN yield rates. For nitrate conversion and TAN yield time is cumulative time of CPE. g) Areal (normalized to GPM area) and h) volumetric (normalized to catholyte volume) TAN recovery rates. AEM, GC, and GPM had the same geometric surface area (5.4 cm²). Error bars represent ± one standard deviation from triplicate experiments (n=3) of proof-of-concept ECaB.
Section S6: Donnan dialysis equilibrium calculations

In Donnan dialysis, an ion exchange membrane separates a wastewater (or feed solution) and a saline electrolyte (or receiving solution). Ion exchange between the two solutions is driven by an electrochemical potential gradient for each ion $i$ in the system. More concretely, Donnan dialysis was employed in this work using a concentrated $\text{Cl}^-$ electrolyte as the receiving solution and $\text{NO}_3^-$-rich municipal secondary effluent as the feed solution. When separated by an AEM, feed $\text{NO}_3^-$ ions spontaneously exchange with receiver $\text{Cl}^-$ ions in the synthetic electrolyte, while cation migration is precluded by the fixed positive charges in the membrane.

Section S6.1: System of equations (ion mass balances, electroneutrality, and Donnan equilibrium)

In this section, we provide a system of equations used to model equilibrium conditions for a Donnan dialysis (DD) process. We show general equations which can be applied to any number of ions $i$ in a system where there is a feed solution (FS) and receiving solution (RS) separation by an ion exchange membrane. For the DD process in this work, we consider only $\text{Cl}^-$ and $\text{NO}_3^-$ because the monovalent-selective anion exchange membrane (AEM) used in ECaB experiments was selective against $\text{SO}_4^{2-}$ migration and rejected cation migration. Fig. S31 shows predicted equilibrium conditions for DD as a function of feed to receiving solution volume ratios.

1. Mass balance

$$C_{i,FS,0}V_{FS} + C_{i,RS,0}V_{RS} = C_{i,FS,\text{equil}}V_{FS} + C_{i,RS,\text{equil}}V_{RS}$$ \hspace{1cm} (Equation S6.1.1)

2. Electroneutrality

$$\sum_i z_i(C_{i,FS,0}V_{FS}) = \sum_i z_i(C_{i,FS,\text{equil}}V_{FS})$$

$$\sum_i z_i(C_{i,RS,0}V_{RS}) = \sum_i z_i(C_{i,RS,\text{equil}}V_{RS})$$ \hspace{1cm} (Equation S6.1.3)
3. Solution phase electrochemical potential equations for Donnan equilibrium

\[ \tilde{\mu}_{i,FS,\text{equil}} = \tilde{\mu}_{i,RS,\text{equil}}. \]  
(Equation S6.1.4)

\[ \mu_i^0 + RT \ln a_{i,FS,\text{equil}} + z_i F \psi_{FS,\text{equil}} = \mu_i^0 + RT \ln a_{i,RS,\text{equil}} + z_i F \psi_{RS,\text{equil}}. \]  
(Equation S6.1.5)

Rearranging Equation S6.1.5 yields an equality between the electrochemical potential difference arising from the activity of each ion \( i \) in feed and receiving streams, and the electrochemical potential difference arising from the electric potential difference across the membrane.

\[ z_i F \psi_{FS,\text{equil}} - z_i F \psi_{RS,\text{equil}} = RT \ln a_{i,RS,\text{equil}} - RT \ln a_{i,FS,\text{equil}}. \]  
(Equation S6.1.6)

Rearranging Equation S6.1.6 yields an equality between the electric potential difference across the ion exchange membrane and the solution phase electrochemical potential difference.

\[ \psi_{FS,\text{equil}} - \psi_{RS,\text{equil}} = \frac{RT}{z_i F} \ln \left( \frac{a_{i,RS,\text{equil}}}{a_{i,FS,\text{equil}}} \right). \]  
(Equation S6.1.7)

Making the approximation that the electric potential difference experienced by each ion \( i \) in the system is the same, the right hand side of Equation S6.1.7 can be used to equate electrochemical potentials of dissimilar ions.

For our example, the electrochemical potentials of \( \text{Cl}^- \) and \( \text{NO}_3^- \) can be equated as in Equations S6.1.8 and S6.1.9.

\[ \frac{RT}{-1*F} \ln \left( \frac{a_{\text{Cl}^-,RS,\text{equil}}}{a_{\text{Cl}^-,FS,\text{equil}}} \right) = \frac{RT}{-1*F} \ln \left( \frac{a_{\text{NO}_3^-,RS,\text{equil}}}{a_{\text{NO}_3^-,FS,\text{equil}}} \right). \]  
(Equation S6.1.8)

\[ \ln \left( \frac{a_{\text{Cl}^-,RS,\text{equil}}}{a_{\text{Cl}^-,FS,\text{equil}}} \right) = \ln \left( \frac{a_{\text{NO}_3^-,RS,\text{equil}}}{a_{\text{NO}_3^-,FS,\text{equil}}} \right). \]  
(Equation S6.1.9)

The activities used in Donnan equilibrium equations were considered for both an ideal model and a Pitzer model based on the concentration of ions in the catholyte.  

\[ a_i = C_i[M] \]  
(Equation S6.1.10)

\[ a_i = \gamma_i C_i[M] \]  
(Equation S6.1.11)
Fig. S33. Equilibrium conditions for Donnan dialysis with secondary effluent wastewater feed and 1 M KCl receiving solution.
Section S7: ECaB process engineering and targets

Section S7.1: Subunit engineered ECaB performance

Fig. S34. Subunit engineered ECaB configuration used to demonstrate improved extraction and conversion rates. To improve extraction from proof-of-concept, we used 2 L (increased from 200 mL) of wastewater (to increase up-concentration) and a commercial serpentine flow field electrolyzer (to reduce mass transport limitations). The resulting catholyte was used in the same commercial electrolyzer to perform Co(DIM)-mediated NO₃RR. TAN recovery was performed in parallel with nitrate conversion using the same experimental setup as in proof-of-concept.
Fig. S35. Photos of the commercial electrolyzer (left) and the electrocatalysis cell and recovery cell in operation (right). Catholyte (C), anolyte (A), and trap (T) chambers and recirculation bottles are labeled.
Fig. S36. Nitrogen mass balance for subunit engineered ECaB (a) Donnan dialysis nitrate extraction and (b) Co(DIM)-mediated NO$_3$RR (nitrate conversion and TAN production) of the resulting catholyte. The dashed horizontal line in panel (a) describes the mass of nitrogen that must be removed from the wastewater to achieve an effluent concentration of 10 mg-N/L; subunit engineered ECaB was able to achieve this concentration in 24 h with 2 L of wastewater feed. 67.5% of nitrate was extracted in 24 h, and 80.8% of the extracted nitrate was converted to TAN in 8 h of CPE.
Fig. S37. Rates of nitrate extraction (orange) and TAN production (green) expressed as (a) flux of nitrogen and (b) partial current density. In Panel (b), extraction partial current density is an effective ionic current density of nitrate crossing the AEM from wastewater to catholyte (balanced by an equal and opposite flux of chloride crossing the AEM from catholyte to wastewater); no external current was applied during extraction. (c) Nitrate extraction efficiency and TAN yield. (d) Area-normalized volume of wastewater treated and farmland serviced with (NH₄)₂SO₄ fertilizer. Farmland serviced was calculated by assuming a rate of 72 kg-N hectare⁻¹ year⁻¹: the average fertilizer application rate of crops in the United States.¹²
Fig. S38. (a) Rates, (b) efficiencies, and (c) energy consumption of nitrate extraction, TAN production, and TAN recovery in proof-of-concept ECaB (orange) and subunit engineered ECaB (purple). These data are the same that appear in Extended Data Tables 1, 3, and 4. Error bars represent ± one standard deviation from triplicate experiments (n=3) for proof-of-concept ECaB. Data points for subunit engineered ECaB do not have error bars because only one experiment was performed.
Section S7.2: Simplified cost assessment

Our cost assessment used the flux of $^{15}NO_3^-$ from a municipal wastewater treatment plant processing $10^7 gal_{wastewater} day^{-1}$ (the size of a large municipal wastewater treatment facility)\textsuperscript{13} with 28 mg-NO$_3$-N L$^{-1}$ as the basis for electricity consumption (a total NO$_3$RR current to convert all nitrate to TAN), chemical inputs (NaCl for nitrate extraction and H$_2$SO$_4$ for TAN recovery), and revenue ((NH$_4$)$_2$SO$_4$ fertilizer sales).

NO$_3$RR overpotential ($\eta_{NO3RR}$) was calculated using the standard reduction potential of NO$_3$RR to ammonia (+0.7 V$\textsubscript{RHE}$)\textsuperscript{14} and the Nernst equation assuming a steady state pH of 10 to facilitate TAN recovery by membrane stripping. Total charge required was calculated assuming a removal efficiency of 64.2% such that the effluent concentration was 10 mg-NO$_3$-N L$^{-1}$. OER overpotential ($\eta_{OER}$) was calculated using the standard reduction potential of OER (+1.23 V$\textsubscript{RHE}$) and the Nernst equation assuming a steady state pH of 1.5 observed in subunit engineered ECaB experiment. Based on the FE$_{TAN}$, $\eta_{NO3RR}$, and $\eta_{OER}$, the required energy consumption was calculated. Multiplying this value by the electricity cost yielded the operational expenditure (OpEx) for electricity. We also calculated the electricity costs associated with pumping according to Tarpeh et al.\textsuperscript{15}

\begin{equation}
\text{Pumping energy} = \frac{1}{mol\text{ }TAN_{produced}} \left( \frac{tyVH^*}{n_{pump}n_{motor}} \right)
\end{equation}

In equation S7.2.1, $t$ is the duration of pumping wastewater through the extraction cell (24 hours), $y$ is the specific weight of water (9.8 kN m$^{-3}$), $V$ is the flow rate (57 mL min$^{-1}$), $H^*$ is the pump head determined by the length of the serpentine flow path in the extraction cell required to treat $10^7 gal_{wastewater} day^{-1} (1.2 \times 10^7 \text{ m})$, $n_{pump}^*$ is the pump efficiency (assumed 0.4), and $n_{motor}^*$ is the motor efficiency (assumed 0.95).

We subtracted this electricity OpEx value and chemical inputs OpEx value from the revenue of recovered (NH$_4$)$_2$SO$_4$ fertilizer ($2.77$ kg-N$^{-1}$) to establish a yearly cash flow.\textsuperscript{16} To correct for inflation, the yearly cash flow was modified by Equation S7.2.2:
\[
\text{Cash flow(year i)} = (\text{Revenue(year i)} - \text{Electricity costs(year i)} - \text{Chemical costs(year i)} - \ldots \text{CapEx(year i)}) \\
\times 1.03^i
\]

The capital expenditure (CapEx) budget was calculated as the net present value of the cash flow over a ten year reactor lifetime with a discount rate of 10%. The entire CapEx budget was spent (i.e., the unit process is a net zero cost) to establish a total surface area of reactor components (Fig. 6a). Dividing the CapEx budget by the sum of the area-normalized prices of Co(DIM), anode material, and cell hardware (graphite for flow field blocks) yielded a total reactor geometric surface area. Dividing the product of total current and FE\textsubscript{TAN} by the total reactor geometric surface area yielded a TAN partial current density target.

We did not consider the costs of labor, the revenue from water recovery, nor potential regulatory fines from environmental nitrate discharge. Additionally, a cost of electricity above $4.08 \text{ kWh}^{-1}$ forced the process to be a net cost. For this reason, we considered $3 \text{ kWh}^{-1}$, motivated by the U.S. Department of Energy’s 2030 SunShot target.\textsuperscript{7} Table S3 outlines parameters used for the cost assessment.

Table S3. OpEx and CapEx used in simplified cost assessment of ECaB.

<table>
<thead>
<tr>
<th>Expenditure</th>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>OpEx – NO\textsubscript{3}RR electricity</td>
<td>Electricity cost</td>
<td>$3 \text{ kWh}^{-1}$</td>
<td>\textsuperscript{7}</td>
</tr>
<tr>
<td>OpEx – Chemical inputs</td>
<td>Sodium chloride (NaCl)</td>
<td>$6.67 \text{ kg}^{-1}$</td>
<td>\textsuperscript{17}</td>
</tr>
<tr>
<td></td>
<td>Sulfuric acid (H\textsubscript{2}SO\textsubscript{4})</td>
<td>$7.6 \text{ kg}^{-1}$</td>
<td>\textsuperscript{17}</td>
</tr>
<tr>
<td>OpEx – Pumping electricity</td>
<td>Electricity cost</td>
<td>$3 \text{ kWh}^{-1}$</td>
<td>\textsuperscript{15}</td>
</tr>
<tr>
<td>CapEx – Co(DIM)</td>
<td>Cobalt acetate</td>
<td>$23.7 \text{ g}^{-1}$</td>
<td>Sigma</td>
</tr>
<tr>
<td></td>
<td>1,2-bis(3-aminopropylamino)ethane</td>
<td>$40.4 \text{ mL}^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Biacetyl</td>
<td>$33.6 \text{ mL}^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>$11.90 \text{ L}^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Perchloric acid (70 wt%)</td>
<td>$15.6 \text{ mL}^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrobromic acid (48 wt%)</td>
<td>$12.9 \text{ mL}^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Total cost</strong></td>
<td>$3.97 \text{ g}_{\text{Co(DIM)}}^{-1}$ ($8.6 \text{ cm}^{-2}$)</td>
<td></td>
</tr>
<tr>
<td>CapEx – Anode</td>
<td>Platinized titanium mesh</td>
<td>$1.25 \text{ cm}^{-2}$</td>
<td>Fuel Cell</td>
</tr>
<tr>
<td>Store</td>
<td>Material Description</td>
<td>Quantity</td>
<td>Supplier</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>--------------------------------------------------</td>
<td>----------</td>
<td>----------------</td>
</tr>
<tr>
<td>Nickel foil</td>
<td>$\varnothing 7.85 \text{ cm}^2$</td>
<td></td>
<td>McMaster</td>
</tr>
<tr>
<td>CapEx – Membranes</td>
<td>Anion exchange membrane (AEM)</td>
<td>$\varnothing 4.43 \text{ cm}^2$</td>
<td>Selemion</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.16 $\text{ cm}^2_{\text{AEM}} \text{cm}^{-1}_{\text{flow path}}$)</td>
<td></td>
</tr>
<tr>
<td>CapEx – Membranes</td>
<td>Cation exchange membrane (CEM)</td>
<td>$\varnothing 2.95 \text{ cm}^2$</td>
<td>Selemion</td>
</tr>
<tr>
<td>CapEx – Membranes</td>
<td>Gas-permeable membrane (GPM)</td>
<td>$\varnothing 0.54 \text{ cm}^2$</td>
<td>Parker-Hannifin</td>
</tr>
<tr>
<td>CapEx – Cell hardware</td>
<td>Graphite material</td>
<td>$\varnothing 1.8 \text{ cm}^3$</td>
<td>link</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(5.14 $\text{ cm}^3_{\text{graphite}} \text{cm}^{-2}_{\text{flow field}}$)</td>
<td>link</td>
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</table>
Fig. S39. Nitrogen mass balance for ECaB with Co(DIM)-mediated NO\textsubscript{2}RR. (a) Nitrogen mass balance for Donnan dialysis extraction with 2 L of simulated nitrite-bearing wastewater (W; 6.2 mM NaCl, 2 mM NaNO\textsubscript{2}) and 50 mL of catholyte (C; 1 M KCl, 8 mM Co(DIM). The extraction cell configuration and operation were the same as for subunit engineered ECaB with real wastewater. (b) Nitrogen mass balance for Co(DIM)-mediated nitrite conversion to TAN with concurrent TAN recovery. The conversion cell and trap cell configuration and operation were the same as for the subunit engineered ECaB with real wastewater, except that the constant potential –1.05 V vs. Ag/AgCl was applied for 15 minute increments instead of 1 h increments because Co(DIM)-mediated NO\textsubscript{2}RR is significantly faster than Co(DIM)-mediated NO\textsubscript{3}RR.
<table>
<thead>
<tr>
<th>ref</th>
<th>Wastewater</th>
<th>Extraction mechanism</th>
<th>Nitrate extraction efficiency ($\eta_{\text{NO}_3\text{-Extraction}}$)</th>
<th>Nitrate extraction rate</th>
<th>Nitrate extraction energy consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>*This work</td>
<td>Secondary effluent (2 mM nitrate)</td>
<td>Donnan dialysis (1 M KCl receiver solution)</td>
<td>$81.3 \pm 3.3%$ at 24 h, $98.1 \pm 0.3%$ at 96 h</td>
<td>$34.6 \pm 1.7$ at 24 h, $10.4 \pm 0.1$ at 96 h</td>
<td>$23.0 \pm 1.3$ at 24 h, $7.8 \pm 0.1$ at 96 h, $0$ (39.0 ± 0.2 considering all subunits)</td>
</tr>
<tr>
<td>*This work</td>
<td>Secondary effluent (2 mM nitrate)</td>
<td>Donnan dialysis (1 M KCl receiver solution)</td>
<td>67.5% at 24 h</td>
<td>151.6 at 24 h</td>
<td>18.2 at 24 h, 0 (48.2 considering all subunits)</td>
</tr>
<tr>
<td>18</td>
<td>Secondary effluent (2 mM nitrate)</td>
<td>n/a</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td>19</td>
<td>Agricultural tile drainage (0.27 mM nitrate)</td>
<td>Electrodeionization with Polyaniline-Co$_3$O$_4$-carbon nanotube slurry coated on Ti mesh as electrode</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td>20</td>
<td>25 mM NaNO$_3$ in 0.1 M Na$_2$SO$_4$</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>25 mM NaNO$_3$ in 0.5 M Na$_2$SO$_4$</td>
<td>n/a</td>
<td>n/a</td>
<td>n.r.</td>
<td></td>
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<tr>
<td>22</td>
<td>Pharmaceutical industry wastewater (31.1 ± 1.1 mM nitrate)</td>
<td>n/a</td>
<td>n/a</td>
<td>n.r.</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>7.14 mM KNO$_3$</td>
<td>Electrodialysis, 5 cm$^2$ (2 M KNO$_3$, receiver solution)</td>
<td>75.0%</td>
<td>542.4</td>
<td>n.r.</td>
</tr>
</tbody>
</table>

*Equations used to calculate ECaB performance metrics in this work are provided in Section S.5.1.*
Table S5. Efficiency, rate, and energy comparison to literature: Nitrate conversion by NO₃RR

<table>
<thead>
<tr>
<th>ref</th>
<th>Wastewater</th>
<th>Electrode/catalyst (Geometric surface areas)</th>
<th>Nitrate conversion $X_{\text{NO}_3^{-} \text{Conversion}}$</th>
<th>FE to TAN</th>
<th>Nitrate conversion rate $\mu g \text{N cm}^{-2} \text{geometric h}^{-1}$</th>
<th>Nitrate conversion energy consumption $mg \text{N L}^{-1} \text{day}^{-1}$ kWh kg-N$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>Secondary effluent (2 mM nitrate concentrated to 5.8 mM)</td>
<td>Co(DIM), 5.4 cm² glassy carbon plate cathode</td>
<td>62.0 ± 1.0% at 96 h (30 h cumulative CPE)</td>
<td>57.4 ± 0.2% at 96 h (30 h cumulative CPE)</td>
<td>20.0 ± 0.2 at 96 h (30 h cumulative CPE)</td>
<td>59.1 ± 1.9 at 96 h (30 h cumulative CPE)</td>
</tr>
<tr>
<td>19</td>
<td>Secondary effluent (2 mM nitrate concentrated to 54 mM)</td>
<td>Co(DIM), 10 cm² graphite serpentine flow field</td>
<td>80.8 at 48 h (8 h cumulative CPE)</td>
<td>329.0 at 48 h (8 h cumulative CPE)</td>
<td>329.0 at 48 h (8 h cumulative CPE)</td>
<td>2193.5 at 48 h (8 h cumulative CPE)</td>
</tr>
<tr>
<td>20</td>
<td>Secondary effluent (2 mM nitrate)</td>
<td>Co(DIM), 64 cm² 316 SS mesh cathode</td>
<td>70.5 ± 2.7% at 42 h</td>
<td>10-15%</td>
<td>1.9</td>
<td>21</td>
</tr>
<tr>
<td>21</td>
<td>Agricultural tile drainage (0.27 mM nitrate concentrated to 2.45 mM)</td>
<td>Polyaniline-Co₃O₄-carbon nanotube slurry coated on Ti mesh</td>
<td>n.r.</td>
<td>28%</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td>22</td>
<td>Printing wastewater (14.9 mM nitrate)</td>
<td>Electrodeposited Co on Ti mesh (16 cm²)</td>
<td>100% at 3 h</td>
<td>43.7%</td>
<td>n.r.</td>
<td>n.r.</td>
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<tr>
<td>23</td>
<td>Pharmaceutical industry wastewater (31.1 ± 1.1 mM nitrate)</td>
<td>CuO@Cu foam</td>
<td>~100%</td>
<td>49.2%</td>
<td>1846 ± 46</td>
<td>n.r.</td>
</tr>
<tr>
<td>24</td>
<td>Oil refining &amp; chemical catalyst manufacturing wastewater (36.1 ± 0.9 mM nitrate)</td>
<td>Ni foam (1.4 m²)</td>
<td>95%</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td>23</td>
<td><strong>1.12 M KNO₃ in 60 wt% NaOH/KOH</strong></td>
<td>Ni mesh (100 cm²), 80 °C</td>
<td>n.r.</td>
<td>70.4%</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
</tbody>
</table>

*Equations used to calculate ECaB performance metrics in this work are provided in Section S.5.1.*
Table S6. Efficiency, rate, and energy comparison to literature: TAN production by NO$_3$RR

<table>
<thead>
<tr>
<th>ref</th>
<th>Wastewater</th>
<th>Electrode/catalyst (Geometric surface areas)</th>
<th>NO$_3$RR product</th>
<th>TAN yield ($Y_{TAN}$)</th>
<th>TAN yield rate</th>
<th>TAN production energy consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>TAN in 1 M KCl</td>
<td>49.0 ± 2.6% at 96 h (30 h cumulative CPE)</td>
<td>15.7 ± 0.9 at 96 h (30 h cumulative CPE)</td>
<td>46.2 ± 0.8 at 96 h (30 h cumulative CPE)</td>
</tr>
<tr>
<td></td>
<td>Secondary effluent (2 mM nitrate concentrated to 5.8 mM)</td>
<td>Co(DIM), 5.4 cm$^2$ glassy carbon plate cathode</td>
<td>TAN in 1 M KCl</td>
<td>49.0 ± 2.6% at 96 h (30 h cumulative CPE)</td>
<td>15.7 ± 0.9 at 96 h (30 h cumulative CPE)</td>
<td>46.2 ± 0.8 at 96 h (30 h cumulative CPE)</td>
</tr>
<tr>
<td></td>
<td>Secondary effluent (2 mM nitrate concentrated to 54 mM)</td>
<td>Co(DIM), 10 cm$^2$ graphite serpentine flow field</td>
<td>TAN in 1 M KCl</td>
<td>82.5 at 48 h (8 h cumulative CPE)</td>
<td>319.6 at 48 h (8 h cumulative CPE)</td>
<td>2130.6 at 48 h (8 h cumulative CPE)</td>
</tr>
<tr>
<td>18</td>
<td>Secondary effluent (2 mM nitrate)</td>
<td>Co(DIM), 64 cm$^2$ 316 SS mesh cathode</td>
<td>TAN in secondary effluent</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td>19</td>
<td>Agricultural tile drainage (0.27 mM nitrate concentrated to 2.45 mM)</td>
<td>Polyaniline-Co$_3$O$_2$- carbon nanotube slurry coated on Ti mesh</td>
<td>TAN in 0.1 M NaCl</td>
<td>n.r.</td>
<td>89.0</td>
<td>n.r.</td>
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<tr>
<td>20</td>
<td>25 mM NaNO$_3$ in 0.1 M Na$_2$SO$_4$</td>
<td>Electrodeposited Co on Ti mesh (16 cm$^2$)</td>
<td>TAN in NaNO$_3$ and 0.1 M Na$_2$SO$_4$</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td>21</td>
<td>Printing wastewater (14.9 mM nitrate)</td>
<td>Electrodeposited Co on Ti mesh (16 cm$^2$)</td>
<td>TAN in printing wastewater</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td>22</td>
<td>Oil refining &amp; chemical catalyst manufacturing wastewater (36.1 ± 0.9 mM nitrate)</td>
<td>Ni foam (1.4 m$^2$)</td>
<td>TAN in manufacturing wastewater</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td>23</td>
<td>$1.12 \text{ M KNO}_3$ in 60 wt% NaOH/KOH</td>
<td>Ni mesh (100 cm$^2$), 80 °C</td>
<td>TAN in 60 wt% NaOH/KOH</td>
<td>n.r.</td>
<td>11494</td>
<td>n.r.</td>
</tr>
</tbody>
</table>

508 *Equations used to calculate ECaB performance metrics in this work are provided in Section S.5.1.*
<table>
<thead>
<tr>
<th>ref</th>
<th>Wastewater</th>
<th>Recovery mechanism</th>
<th>Recovered product</th>
<th>TAN recovery efficiency ((\eta_{\text{TAN Recovery}}))</th>
<th>TAN recovery rate (\mu g , N , cm^{-2}h^{-1})</th>
<th>TAN recovery rate (mg , N , L^{-1} \text{day}^{-1})</th>
<th>TAN recovery energy consumption (\text{kWh kg-N}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Secondary effluent (2 mM nitrate concentrated to 5.8 mM)</td>
<td>Electrochemical basification + Membrane stripping (5.4 cm² membrane area)</td>
<td>((\text{NH}_4)_2\text{SO}<em>4</em>{aq}) in (0.1 \text{ M } \text{H}_2\text{SO}<em>4</em>{aq})</td>
<td>91.0 ± 2.1% at 96 h (*Overall N recovery: 42.6 ± 1.4%)</td>
<td>6.0 ± 0.2 at 96 h</td>
<td>18.1 ± 0.2 at 96 h</td>
<td>90.0 ± 2.7 at 96 h (cumulative)</td>
</tr>
<tr>
<td></td>
<td>Secondary effluent (2 mM nitrate concentrated to 54 mM)</td>
<td>Electrochemical basification + Membrane stripping (5.4 cm² membrane area)</td>
<td>((\text{NH}_4)_2\text{SO}<em>4</em>{aq}) in (0.1 \text{ M } \text{H}_2\text{SO}<em>4</em>{aq})</td>
<td>22.8% at 48 h (*Overall N recovery: 11.0%)</td>
<td>45.8 at 48 h</td>
<td>169.6 at 48 h</td>
<td>295.3 at 48 h (cumulative)</td>
</tr>
<tr>
<td>18</td>
<td>Secondary effluent (2 mM nitrate)</td>
<td>Electrochemical basification + Membrane stripping (64 cm² membrane area)</td>
<td>((\text{NH}_4)_2\text{SO}<em>4</em>{aq}) in (0.1 \text{ M } \text{H}_2\text{SO}<em>4</em>{aq})</td>
<td>Overall N recovery: 53.6 ± 2.8%</td>
<td>1.3</td>
<td>15.9</td>
<td>340 ± 30 (cumulative)</td>
</tr>
<tr>
<td>19</td>
<td>Agricultural tile drainage (0.27 mM nitrate concentrated to 2.45 mM)</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td>20</td>
<td>25 mM NaNO₃ in 0.1 M Na₂SO₄</td>
<td>Electrochemical basification + Membrane stripping (16 cm² membrane area)</td>
<td>((\text{NH}_4)_2\text{SO}<em>4</em>{aq}) in (1 \text{ M } \text{H}_2\text{SO}<em>4</em>{aq})</td>
<td>Overall N recovery: 83.8% at 3 h</td>
<td>n.r.</td>
<td>n.r.</td>
<td>155</td>
</tr>
<tr>
<td>21</td>
<td>25 mM NaNO₃ in 0.5 M Na₂SO₄</td>
<td>Electrochemical basification + Membrane stripping (4 cm² membrane area)</td>
<td>((\text{NH}_4)<em>2\text{SO}<em>4</em>{aq}) in acidified 0.5 M Na₂SO₄</em>{aq}</td>
<td>Overall N recovery: ∼100%</td>
<td>733 ± 42</td>
<td>n.r.</td>
<td>140.6 ± 13.7</td>
</tr>
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<td></td>
<td>Pharmaceutical industry wastewater (31.1 ± 1.1 mM nitrate)</td>
<td>Electrochemical basification + Membrane stripping (4 cm² membrane area)</td>
<td>((\text{NH}_4)<em>2\text{SO}<em>4</em>{aq}) in acidified 0.5 M Na₂SO₄</em>{aq}</td>
<td>n.r.</td>
<td>916 ± 27</td>
<td>n.r.</td>
<td>n.r.</td>
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<tr>
<td>22</td>
<td>Oil refining &amp; chemical catalyst manufacturing</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td></td>
<td>wastewater (36.1 ± 0.9 mM nitrate)</td>
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</tr>
<tr>
<td>23</td>
<td>$1.12 \text{ M } \text{KNO}_3 \text{ in } 60 \text{ wt% } \text{NaOH/KOH}$</td>
<td>Carrier gas stripping</td>
<td>$\text{NH}_3(\text{aq})$, $\text{NH}_4\text{HCO}_3$, $(\text{NH}_4)_2\text{SO}_4$</td>
<td>~100%</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
</tbody>
</table>

*Equations used to calculate ECaB performance metrics in this work are provided in Section S.5.*
References


