Harnessing Photoelectrochemistry for Wastewater Nitrate Treatment Coupled with Resource Recovery

Luisa Barrera, Rohini Bala Chandran

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Wastewater is a misplaced resource well suited to recover nutrients, value-added chemicals, energy, and clean water. A photoelectrochemical device is proposed to transform wastewater nitrates to ammonia and nitrous oxide, coupled with water oxidation. Numerical models were developed to quantify the dependence of process efficiencies and nitrogen-removal rates on light absorber band gaps, electrocatalytic kinetic parameters, competing oxygen reduction and hydrogen evolution reactions, and the reacting nitrate species concentrations that affect the mass-transfer limited current densities. With a single light-absorber and state-of-the-art catalysts, optimal solar-to-chemical efficiencies of 7% and 10% and nitrogen-removal rates of 260 and 395 gN m⁻² day⁻¹ are predicted for nitrate reduction to ammonia and nitrous oxide respectively. The influence of competing reactions on the performance depends on the nitrate concentration and band gap of the light absorber modeled. Oxygen reduction is more dominant than hydrogen evolution to compete with the nitrate reduction reaction, but is mass-transfer limited. Even with kinetic parameters that enhanced the driving forces for the competing reactions, the performance is only minimally affected by these reactions for optimally selected band gaps and nitrate concentrations larger than 100 mM. Theoretically predicted peak nitrogen removal rates and specific energy intensities are competitive with reported estimates for bioelectrochemical and Sharon-Anammox processes for ammonia recovery and nitrogen removal respectively. This result, together with the added benefit of harnessing sunlight to produce value-added products, indicates promise in the photoelectrochemical approach as a tertiary pathway to recover nutrients and energy from wastewater nitrates.
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Luisa Barrera and Rohini Bala Chandran*

Abstract

Wastewater is a misplaced resource well suited to recover nutrients, value-added chemicals, energy, and clean water. A photoelectrochemical device is proposed to transform wastewater nitrates to ammonia and nitrous oxide, coupled with water oxidation. Numerical models were developed to quantify the dependence of process efficiencies and nitrogen-removal rates on light absorber band gaps, electrocatalytic kinetic parameters, competing oxygen reduction and hydrogen evolution reactions, and the reacting nitrate species concentrations that affect the mass-transfer limited current densities. With a single light-absorber and state-of-the-art catalysts, optimal solar-to-chemical efficiencies of 7% and 10% and nitrogen-removal rates of 260 and 395 gN m⁻² day⁻¹ are predicted for nitrate reduction to ammonia and nitrous oxide respectively. The influence of competing reactions on the performance depends on the nitrate concentration and band gap of the light absorber modeled. Oxygen reduction is more dominant than hydrogen evolution to compete with the nitrate reduction reaction, but is mass-transfer limited. Even with kinetic parameters that enhanced the driving forces for the competing reactions, the performance is only minimally affected by these reactions for optimally selected band gaps and nitrate concentrations larger than 100 mM. Theoretically predicted peak nitrogen removal rates and specific energy intensities are competitive with reported estimates for bioelectrochemical and Sharon-Anammox processes for ammonia recovery and nitrogen removal respectively. This result, together with the added benefit of harnessing sunlight to produce value-added products, indicates promise in the photoelectrochemical approach as a tertiary pathway to recover nutrients and energy from wastewater nitrates.

TOC Graphic

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1. Introduction

Excessive anthropogenic production of nitrogen fertilizers combined with fossil-fuel combustion has significantly disrupted the natural nitrogen cycle\(^1\)–\(^3\), leading to the contamination of groundwater and other surface-water bodies with various reactive forms of nitrogen—nitrates (NO\(_3^-\)), nitrites (NO\(_2^-\)), ammonia (NH\(_3\)), ammonium (NH\(_4^+\)) and organic nitrogen. These contaminants result in environmental threats such as algal blooms, suffocation of aquatic wildlife, and health risks in humans, e.g. excessive amounts of nitrates in drinking water causes methemoglobinemia (“blue baby” syndrome)\(^4\)–\(^8\). While several strategies have been reported to recover value-added products — energy from biogas and chemicals including biopolymers, bio-oils, and biochar from organic contaminants — far less emphasis has been placed on nutrient (i.e. nitrogen) and energy recovery from nitrogen contaminants\(^9\)–\(^12\).

This study focuses on evaluating the feasibility of a photoelectrochemical approach to recover nitrogen nutrients from NO\(_3^-\) contaminants present in ion-exchange brines\(^13\)–\(^16\) and treated wastewater\(^11\),\(^17\)–\(^19\). Biological nitrification-denitrification treatment processes are attractive as they utilize microbes to consume and remove the excess nutrients\(^20\),\(^21\). However, these processes are energy intensive\(^22\), not effective in effluent streams that harbor conditions unsuitable for microbial growth\(^3\),\(^23\), and have not been optimized for resource recovery\(^12\). Ion-exchange\(^5\),\(^24\),\(^25\), electrodialysis\(^26\),\(^27\), and reverse osmosis\(^28\),\(^29\) are used to treat nitrates (and other ions) at an industrial scale for drinking water applications, but result in the production of a secondary nitrate-concentrated brine that requires further treatment\(^30\). Hence, there is an increasing demand to develop wastewater treatment technologies to harness renewable energy, to be effective for a wide range of effluent stream conditions and to facilitate resource recovery in the form of nutrients and energy. To meet these critical needs, photoelectrochemical devices offer the potential to couple...
sunlight with electron-transfer reactions to treat and transform nitrogen-contaminants to value-added chemicals and therefore facilitate nitrogen recovery.

Prior work has provided theoretical limits for the solar-to-fuel energy conversion efficiencies and established guidelines to select semiconductor and co-catalysts/electrocatalysts to optimize the efficiency for photoelectrochemical water splitting devices, which generate hydrogen and oxygen from water using light absorbers and electrocatalysts. However, the same extent of understanding is not available for photoelectrochemical nitrate treatment devices. Photocatalytic nitrate reduction has been investigated predominantly with TiO$_2$-based light absorbers with NO$_3^-$ reduction often paired with sacrificial hole-scavengers (methanol, oxalic acid, and formic acid). However, TiO$_2$ limits process efficiencies due to the low sunlight absorption and the presence of hole-scavengers lead to toxicity concerns for water treatment applications. Comprehensive reviews have been reported on electrochemical denitrification, i.e. NO$_3^-$ to N$_2$ conversion, including investigations on metallic and bimetallic electrocatalysts for NO$_3^-$ to N$_2$ and NH$_3$ conversion, and studies that probe fundamental reaction mechanisms. However, the focus in a majority of these studies has been on electrocatalytically reducing NO$_3^-$ to N$_2$, which poses formidable kinetic (reactivity and selectivity) challenges. Therefore, there is a lack of knowledge on the ideal performance limits and the impacts of materials parameters on the performance of a photoelectrochemical approach to recover nitrogen nutrients from wastewater.

The objective of this study is to theoretically predict the solar-to-chemical energy conversion efficiencies and the rate of recovery of nitrogen for a photoelectrochemical device that is operating on treated wastewater with predominantly nitrate contaminants (Figure 1). A notable innovation introduced in the modeling approach developed is the capability to account for the effects of competing hydrogen evolution and the oxygen reduction reactions that can compete with
the desired nitrate reduction reaction at the cathode, within a simplified, yet powerful, equivalent
circuit modeling framework. The model developed is used to obtain the impacts of material
parameters, including the light-absorber band gaps, electrocatalyst exchange current densities and
charge-transfer coefficients for the desired and the competing reactions, and operating nitrate
concentration in the waste stream, on all the performance metrics. These results are interpreted to
provide guidelines to select materials for the light absorbers and electrocatalysts to maximize
resource (nitrogen) recovery. Furthermore, the predicted performance metrics are used to compare
the proposed approach with the state-of-the-art nitrogen removal/recovery technologies – the
Sharon-Annamox process\textsuperscript{61,62} and ammonia stripping using electrochemical flow reactors\textsuperscript{63}.

2. Photoelectrochemical Device for Wastewater Nitrate Treatment

In this work, we propose a photoelectrochemical device to pair water oxidation with nitrate
reduction (Figure 1). A photoactive semiconductor anode absorbs incident sunlight and is
electrically connected to the cathode. The holes generated at the photoanode surface effect the
oxygen evolution reaction (OER) while at the cathode surface the electrons effect the nitrate
reduction reaction (NO\textsubscript{3}RR) to the desired products including NH\textsubscript{3}/NH\textsubscript{4}\textsuperscript{+} and N\textsubscript{2}O. An ion-
exchange membrane may be present to facilitate ion transport while preventing gas crossover
between the electrodes. Compared to the removal of NO\textsubscript{3} contaminants as N\textsubscript{2}, the transformation
to NH\textsubscript{3}/NH\textsubscript{4}\textsuperscript{+} and N\textsubscript{2}O recovers the N-nutrients and upgrades the energetic value of the reactive-
nitrogen contaminant species. Aqueous NH\textsubscript{3}/NH\textsubscript{4}\textsuperscript{+} can be reused as a fertilizer and/or oxidized to
generate electricity in an ammonia fuel-cell, and gaseous NH\textsubscript{3} can be used as a fuel to generate
heat and produce electricity\textsuperscript{64–66}. Despite being a potent greenhouse gas, N\textsubscript{2}O is also a powerful
oxidizer, especially for the combustion of rocket-fuel and biogas and for supercharging
applications\textsuperscript{67,68}. It increases the energy released during the combustion of CH\textsubscript{4} by 37% as
compared to using O\textsubscript{2} as an oxidizer, and therefore has been previously considered as a viable end-product for energy recovery\textsuperscript{67,71}.

As an idealized starting point for our analyses, we assumed the presence of predominantly NO\textsubscript{3}\textsuperscript{−} contaminants in the waste stream. Such an assumption could be reasonable for a tertiary treatment process designed for resource recovery from nitrogen-contaminants in pre-treated wastewater from municipal wastewater treatment plants, ion-exchange brines and other industrial processes\textsuperscript{11,13–19}.

**Figure 1:** Schematic of a photoelectrochemical device for treating wastewater nitrate contaminants. Selective water oxidation at the photoanode and the NO\textsubscript{3}\textsuperscript{−} reduction pathways to form NH\textsubscript{3} (R1), N\textsubscript{2}O (R2) and N\textsubscript{2} (R3) are depicted. All the standard potentials, \(E^0\), for aqueous solutions at 25°C are reported vs. NHE based on a 1 atm standard state for H\textsubscript{2}. Unless otherwise mentioned all species are in the aqueous phase\textsuperscript{69,70}. A negative \(E^0\) for a net reaction indicates that it is thermodynamically uphill, while a positive \(E^0\) indicates reaction spontaneity.

<table>
<thead>
<tr>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2 \text{OH} \rightarrow \frac{1}{2} \text{O}_2(g) + \text{H}_2\text{O} + 2e^-)</td>
<td>(\text{NO}_3^- + 7 \text{H}_2\text{O} + 8 e^- \rightarrow \text{NH}_3(g) + 9 \text{OH}^-)</td>
</tr>
<tr>
<td><strong>Net Reaction, R1:</strong></td>
<td>(\text{NO}_3^- + 3 \text{H}_2\text{O} \rightarrow \text{NH}_3(g) + \text{OH}^- + 2 \text{O}_2)</td>
</tr>
<tr>
<td>(2 \text{OH} \rightarrow \frac{1}{2} \text{O}_2(g) + \text{H}_2\text{O} + 2e^-)</td>
<td>(\text{2 NO}_3^- + 5 \text{H}_2\text{O} + 8 e^- \rightarrow \text{N}_2\text{O}(g) + 10 \text{OH}^-)</td>
</tr>
<tr>
<td><strong>Net Reaction, R2:</strong></td>
<td>(2 \text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{N}_2\text{O}(g) + 2 \text{OH}^- + 2 \text{O}_2)</td>
</tr>
<tr>
<td>(2 \text{OH} \rightarrow \frac{1}{2} \text{O}_2(g) + \text{H}_2\text{O} + 2e^-)</td>
<td>(\text{2 NO}_3^- + 6 \text{H}_2\text{O} + 10 e^- \rightarrow \text{N}_2(g) + 12 \text{OH}^-)</td>
</tr>
<tr>
<td><strong>Net Reaction, R3:</strong></td>
<td>(2 \text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{N}_2(g) + 2 \text{OH}^- + \frac{5}{2} \text{O}_2)</td>
</tr>
</tbody>
</table>
3. Theory & Numerical Model

A zero-dimensional (0-D), equivalent circuit model was developed to determine operating current densities and potentials, where the semiconductor light absorber was modeled as an ideal diode in series with the electrochemical reactions, which were modeled as variable resistors to account for the electrocatalyst current-overpotential behavior\(^{31-38}\) (Figure 1). A nomenclature of symbols is included in the ESI. For the electrochemical reactions, kinetic and the mass-transfer potential losses were considered. While selective oxidation of water (OER) was assumed to occur at the anode (Eq. (1a)), non-selective reduction reactions were modeled at the cathode by considering parallel current pathways and by enforcing potential equality (Eq. (1a)) in the parallel branches; the overall operating potential of the diode is given by Eq. (2).

\[
V_{\text{anode}} = \text{E}_{\text{eq}, \text{OER}} + \eta_{\text{OER}} \quad \text{(1a)}
\]

\[
V_{\text{cathode}} = \begin{cases} 
\text{E}_{\text{eq}, \text{NO3RR}} + \eta_{\text{NO3RR}} \\
\text{E}_{\text{eq}, \text{HER}} + \eta_{\text{HER}} \\
\text{E}_{\text{eq}, \text{ORR}} + \eta_{\text{ORR}} 
\end{cases} \quad \text{(1b)}
\]

\[
V_{\text{op}} = V_{\text{anode}} - V_{\text{cathode}} \quad \text{(2)}
\]

At the anode, selective OER is justified by the low likelihood of oxidizing nitrogen-products (N\(_2\)O and NH\(_3\) especially for pH>12\(^{23,72}\)). However, at the cathode, in addition to the desired nitrate reduction reaction (NO\(_3\)RR), competing hydrogen evolution (HER) and oxygen reduction (ORR) reactions were also modeled. The HER has been reported to compete with the NO\(_3\)RR in prior work with Cu catalysts\(^{3,57,72}\); the ORR was considered due to the O\(_2\) produced at the anode, which can crossover and react at the cathode surface.

The Nernstian potential, \(E_{\text{eq}}\), was included (Eq. (3)) as the minimum electrical load at the cathode and the anode.

\[
E_{\text{eq}} = E^0 + \frac{R T}{n_e F} \ln \left( \frac{a_{O}^{\gamma_{O}}}{a_{R}^\gamma_{R}} \right) \quad \text{(3)}
\]
Figure 2: Equivalent circuit diagram to model the operation and performance of the photoelectrochemical device in Figure 1. The semiconductor light-absorber was modeled as a photodiode and the electrochemical reactions as variable resistors with minimum electrical loads corresponding to the thermodynamic potentials for the corresponding reactions. Selective oxygen evolution reaction (OER) at the anode and parallel reactions were modeled at the cathode including the desired NO3RR, and the competing HER and ORR. Desired reactions in the circuit are indicated by the solid lines and the undesired and competing reactions at the cathode are indicated by the dashed lines.

Current conservation, Eq. (4), was satisfied in the circuit, while taking into account the parallel and competing reactions occurring at the cathode. The sign convention adopted implements the reduction current densities to be negative and the oxidation current density to be positive.

\[ j_{op} = j_{OER} = - \sum_{i=NO3RR,ORR,HER} j_i \]  

Light Absorber: The semiconductor light absorber was modeled as a diode with the pertinent governing equations and key assumptions summarized in Table 1\textsuperscript{31–38}. Ideal diode behavior with only radiative recombination (Eqs. (5)-(7)) and a large optical path length was assumed to keep the analyses general and to analyze a wide range of light absorber bandgaps. However, the trends predicted for the impacts of the material band gaps on the performance metrics are expected to be valid even with more realistic recombination models.
Table 1: List of the governing equations for the semiconductor light absorber in the equivalent circuit (0-D) model

<table>
<thead>
<tr>
<th>Physics modeled</th>
<th>Governing equations and key assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current-potential behavior of the semiconductor</td>
<td>Shockley-Queisser detailed-balance model(^{36})</td>
</tr>
<tr>
<td></td>
<td>( j_{\text{op}} = j_{\text{sc}} - j_{\text{rr}} \left( \frac{q_e V_{\text{op}}}{e^{n_d k_B T} - 1} \right) ) (5)</td>
</tr>
<tr>
<td>(i)</td>
<td>Optically thick semiconductor absorbs all the above-band-gap photons to ensure that current density is not limited by the material design, i.e. planar electrodes(^{36}), photocatalytic particle suspension reactors(^{33}), nanowires(^{73}) etc.</td>
</tr>
<tr>
<td>(ii)</td>
<td>Negligible optical losses due to reflection at the surface of the light absorber to keep the analysis generic and applicable over a wide range of material bandgaps</td>
</tr>
<tr>
<td>(iii)</td>
<td>Ideal diode with only radiative recombination dictated by the rate of thermal emission of photon at ambient temperature, ( T = 298.15 ) K</td>
</tr>
</tbody>
</table>

Short-circuit current density, \( j_{\text{sc}} \)

\[ j_{\text{sc}} = q_e \int_{\nu_{g} = E_g / k_B T}^{\infty} \phi_{\text{solar}}(\nu) \, d\nu \] (6)

(i) Electron-hole (\( e^-/h^+ \)) pairs are generated by each and every incident photon with energy larger than its band gap of \( E_g \)

(ii) Excited-state charge carriers rapidly thermalize to the band edges and each absorbed photon produces only one \( e^-/h^+ \) pair

Radiative recombination current density, \( j_{\text{rr}} \)

\[ j_{\text{rr}} = 2 q_e \left( \frac{2 \pi}{c^2} \right) \int_{\nu}^{\infty} \frac{v^2}{\nu^2} \frac{h \nu}{e^{h \nu / k_B T} - 1} \, d\nu \] (7)

(i) Light absorber is surrounded by a blackbody at the same temperature as that of the diode that is at \( T = 298.15 \) K \(^{36}\)

Electrochemical Reactions: Potential losses for the electrochemical reactions included the mass-transfer (\( \eta_{i,\text{mt}} \)) and the kinetic (\( \eta_{i,k} \)) overpotentials for all the redox reactions considered, i.e. \( i = \text{OER, NO3RR, HER, and ORR (Eqs. (8) and (9))} \).

\[ \eta_i = \eta_{i,k} + \eta_{i,\text{mt}} \] (8)

The mass-transfer overpotential was included to account for the bulk concentration-dependent limiting current densities for all redox species (\( \text{NO}_3^-/\text{NO}_2^- \) for NO3RR, \( \text{H}_2\text{O}/\text{H}_2 \) for HER, and \( \text{O}_2/\text{OH} \) for ORR) except for the OER. For the OER, this mass-transfer overpotential component in Eq. (8) is assumed to be negligibly small because of the large concentration of the reacting species, \( c_{\text{H}_2\text{O}} = 55.5 \) M (pH = 1) and \( c_{\text{OH}^-} = 1 \) M (pH = 14). Equation (9) accounts for the mass-transfer overpotential,
9

\[ \eta_{i,mt} = \frac{RT}{Fn_e} \ln \left( \frac{1 - \frac{j_i}{j_{i,c}}}{\nu_{l,c}} \right) \left( \frac{1 - \frac{j_i}{j_{i,a}}}{\nu_{l,a}} \right) \]  

(9)

where, \( j_i \) is the limiting current density for the cathodic (c) and anodic (a) half-reactions. Limiting current densities were calculated assuming diffusion-limited species transport (Eq. (10)) of the oxidized (O) or reduced species (R), with a concentration boundary layer thicknesses of 10 µm,

\[ \delta_{BL} = 10 \mu m, \] 

which is a reasonable assumption for planar electrode architectures with laminar flow regime\(^7\),

\[ j_{i,a/c} = \pm \frac{n_e F D_{R/O} C_{R/O}}{\delta_{BL} \nu_{R/O}} \]  

(10)

Butler-Volmer equations were applied to model reversible electron transfer reactions (Eq. (11)) and irreversible cathodic reactions (Eq. (12)),

\[ j_i = j_{0,ref,i} \left( \frac{C_{R,bulk}}{C_{R,bulk,ref}} \right)^{\frac{v_{R,c}}{n_e}} \left( \frac{C_{O,bulk,ref}}{C_{O,bulk}} \right)^{\frac{v_{O,a}}{n_e}} \exp \left( \frac{\alpha_{a,i} \eta_{i,k}}{RT/F} \right) - \exp \left( \frac{-\alpha_{c,i} \eta_{i,k}}{RT/F} \right) \]  

(11)

\[ j_i = j_{0,ref,i} \left( \frac{C_{O,bulk}}{C_{O,bulk,ref}} \right)^{1-\frac{v_{R,c}}{n_e}} \left( -\exp \left( \frac{-\alpha_{c,i} \eta_{i,k}}{RT/F} \right) \right) \]  

(12)

where, \( j_{0,ref,i} \) is the reference surface- and concentration-dependent exchange current density of the \( i^{th} \) reaction (for a selected electrocatalyst, the larger the \( j_{0,i} \) value, the faster the rate is for both the anodic and cathodic directions of the reversible redox reactions); \( \alpha_a \) and \( \alpha_c \) are the charge-transfer coefficients indicating the symmetry of the activation barrier for the reaction. Equation (11) was applied to model the kinetics for OER, HER, and ORR, whereas Eq. (12) was used for NO3RR. A literature review was performed to identify the state-of-the-art catalysts for OER and NO3RR, based on which the kinetic parameters (\( j_{0,ref,i}, \alpha_{c,i}, \alpha_{a,i} \)) were determined for these reactions (Table 2). For NO3RR, catalysts were selected based on satisfying two criteria: (a) the availability of kinetic parameters, or cyclic voltammograms or Tafel plots based on which kinetic parameters can be extracted, and (b) the inclusion of product composition analyses to determine
Table 2: Reactions modeled with relevant pH, reference exchange current density, $j_{0,\text{ref}}$; charge transfer coefficients, $\alpha_c$ and $\alpha_a$; N/A for the charge-transfer coefficients implies the use of the irreversible equation form (Eq. (12)); bulk reference concentrations, $c_{\text{bulk,ref}}$, extracted from the literature for the catalysts are listed; pH 1 and pH 14 data used for NH$_3$ and N$_2$O production respectively.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>pH</th>
<th>Catalyst</th>
<th>$j_{0,\text{ref}}$ (A m$^{-2}$)</th>
<th>$\alpha_c$</th>
<th>$\alpha_a$</th>
<th>$c_{\text{bulk,ref}}$ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OER$^{33,41,75}$</td>
<td>1</td>
<td>RuO$_2$</td>
<td>$6.68 \times 10^{-4}$</td>
<td>0.1</td>
<td>1</td>
<td>$c_{\text{H}^+} = 1000$; $c_{\text{O}_2,\text{aq}} = 1.3$</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>IrO$_2$</td>
<td>0.48</td>
<td>0.63</td>
<td>0.39</td>
<td>$c_{\text{OH}^-} = 1000$; $c_{\text{O}_2,\text{aq}} = 1.3$</td>
</tr>
<tr>
<td>NO3RR$^{57,58}$</td>
<td>1</td>
<td>Sn-Pt</td>
<td>$2.12 \times 10^{-3}$</td>
<td>0.54</td>
<td>N/A</td>
<td>$c_{\text{NO}<em>3^-} = 10$; $c</em>{\text{H}^+} = 100$</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>Cu</td>
<td>$1.12 \times 10^{-2}$</td>
<td>0.30</td>
<td>N/A</td>
<td>$c_{\text{NO}<em>3^-} = 100$; $c</em>{\text{OH}^-} = 1000$</td>
</tr>
<tr>
<td>HER$^{76,77}$</td>
<td>1</td>
<td>Pt</td>
<td>10</td>
<td>0.5</td>
<td>0.5</td>
<td>$c_{\text{H}^+} = 1000$; $c_{\text{H}_2,\text{aq}} = 0.78$</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>Pt</td>
<td>$10^{-1}$</td>
<td>0.9</td>
<td>0.1</td>
<td>$c_{\text{H}^+} = 100$; $c_{\text{O}_2,\text{aq}} = 1.3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$10^{-5}$</td>
<td></td>
<td></td>
<td>$c_{\text{OH}^-} = 1000$; $c_{\text{O}_2,\text{aq}} = 1.3$</td>
</tr>
</tbody>
</table>

The selectivity to the desired nitrate reduction products$^{49-51,55-58,82,83}$. It was determined that Cu (pH of 14) and Sn-Pt (pH of 1) exhibited high product selectivity for the reduction of NO$_3^-$ to NH$_3$ and N$_2$O respectively$^{57,58}$. The kinetics for the NO3RR was modeled by considering the irreversible reduction of NO$_3^-$ to NO$_2^-$ as the rate-determining step$^{3,23}$.

$$\text{NO}_3^- + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{NO}_2^- + 2 \text{OH}^- \quad E^0 = 0.835 \text{ V v/s NHE} \quad (13)$$

Because of the high product selectivity (> 98%) reported for the state-of-the-art catalysts, we assumed full selectivity in the transformation of NO$_2^-$ to the desired products on the selected catalysts. This is a simplifying assumption to overcome the lack of mechanistic information to model the sequence of elementary steps needed for the various nitrogen-products considered in this study$^3$. In the same pH conditions, the most suitable OER catalysts were identified to be IrO$_2$ (pH = 14) and RuO$_2$ (pH = 1)$^{33,41,75}$.

**Modeling Competing Reactions:** The electrocatalytic parameters ($j_{0,\text{ref,i}}, \alpha_{c,i}, \alpha_{a,i}$) for the competing reactions (ORR and HER) at the cathode were determined such that the impact of the “worst-case” on the efficiency and rates of nitrogen-recovery from the products formed could be
investigated. The largest exchange current density, $j_{0,\text{ref},i}$, for the competing HER was based on
the kinetics reported for Pt at both pH = 1 and pH = 14 (Table 2). The HER was modeled to be
fully reversible with $\alpha_c=\alpha_a=0.5$, as justified by experimentally reported measurements for various
catalysts$^{76,84}$. For the ORR, the $j_{0,\text{ref},i}$ was selected based on reported values for Pt for pH = 1 and
14$^{78-81}$, and the ORR cathodic charge-transfer coefficient was assumed to be $\alpha_c = 0.9$ to model a
surface that is favorable to ORR. In the headspace of the reactor, standard atmospheric conditions
(1 atm, 25°C) with a mole-fraction of 20.9% of O$_2$, trace amounts of H$_2$ (0.5 ppm) and balance N$_2$
was modeled.

Overall, we have a consistent system of algebraic equations (up to 12 when competing
reactions are included) that are simultaneously solved for the variables – $j_{\text{op}}, V_{\text{op}}, \eta_{\text{OER,k}},$
$j_{\text{NO3RR}}, \eta_{\text{NO3RR,k}}, \eta_{\text{NO3RR,mt}}, \dot{j}_{\text{HER}}, \eta_{\text{HER,k}}, \eta_{\text{HER,mt}}, \dot{j}_{\text{ORR}}, \eta_{\text{ORR,k}}, \eta_{\text{ORR,mt}}$. The system of
equations was solved using the *fsolve* function in Matlab R2018a, with a function tolerance of $10^{-4}$,
an optimality tolerance of $10^{-4}$, a step tolerance of $10^{-4}$, an average finite difference step size of
$1.5 \times 10^{-4}$, and with the default solver algorithm (trust-region dogleg) or in instances when the
convergence was challenging, the Levenberg-Marquardt algorithm was applied$^{85}$.

**Performance Metrics:** The efficiency of converting the incident solar power (1 Sun or
1000 W m$^{-2}$) to the output chemical power was obtained using Eq. (14), where, $\dot{r}$ is the molar flux
of NH$_3$ and N$_2$O produced, and $\Delta G_i^0$ is the standard state free-energy change for the respective
oxidation reactions (Table 2).

$$\eta_{\text{solar-to-chemical},i} = \frac{\dot{r}_i|\Delta G_i^0|}{1000}; i = \text{NH}_3, N_2\text{O} \quad (14)$$

The molar flux, $\dot{r}$, of NH$_3$ and N$_2$O (in mol m$^{-2}$ s$^{-1}$) produced is related to the nitrate reduction
current density, $j_{\text{NO3RR}}$. 11
The oxidation of gaseous NH$_3$ with O$_2$ was modeled, $\Delta g^0_{\text{NH}_3/\text{H}_2\text{O}} = -339$ kJ mol$^{-1}$, whereas gaseous N$_2$O was used as an oxidizer to combust CH$_4$, $\Delta g^0_{\text{CH}_4,\text{N}_2\text{O}/\text{H}_2\text{O}} = -308.7$ kJ mol$^{-1}$. Solar energy conversion efficiencies for the NO$_3^-$-to-N$_2$ transformation is not reported because the N$_2$ produced has to first be reduced to NH$_3$/NH$_4^+$ to facilitate energy recovery, and this step in itself is highly energy intense$^{86,87}$. For comparison, when solar-to-hydrogen efficiencies are computed for photoelectrochemical water-splitting devices, the molar rate of H$_2$ production with $\Delta g^0_{\text{H}_2/\text{H}_2\text{O}} = 237.4$ kJ mol$^{-1}$ is used.

The rate of nitrogen-removal and nitrogen-recovery, $R_N$ (in g$_N$ m$^{-2}$ day$^{-1}$) are equal and directly proportional to the molar flux, $\dot{r}_i$, of the products formed from the nitrate contaminants (Eq. (16)). In Eq. (16), $m_N = 14$ g, is the molar mass of atomic-nitrogen and $t_{\text{day}} = 86400$ s day$^{-1}$. Therefore, a larger solar-to-chemical efficiency is also indicative of improved rates of nitrogen removal/recovery in our analyses.

$$R_N = \dot{r}_i m_N t_{\text{day}}; \ i = \text{NH}_3, \text{N}_2\text{O} \quad (16)$$

The specific energy intensity $E_N$ (in MJ kg$_N^{-1}$) (Eq. (17)) is a measure of the total energy required per unit mass of nitrogen removed and is commonly used as a metric to compare various technologies from an energy-consumption standpoint. The calculation in Eq. (17) assumed that the device steadily operates at the predicted current-density, $j_{\text{op}}$, and operating potential, $V_{\text{op}}$. Therefore, there is lack of dependence on current-density for the $E_N$ calculation, as the current-density term appears both in the numerator (total energy consumption) and the denominator (total mass of nitrogen removed).
4. Results & Discussion

4.1 Composition of Nitrogen-Contaminants in Wastewater

Figure 3 shows the source-dependent variability in the composition of nutrient contaminants, including organic, nitrogen and phosphorous contaminants, for various point-sources of wastewater. Point-sources considered in this study included low-level nuclear wastes, municipal wastewater effluents, ion-exchange brines, power generation, and oil/gas and manufacturing processes. Even though diffuse sources, such as agricultural runoff streams and landfill wastewater, also cause nutrient contamination, they are not included in Figure 3 because the contaminant species and concentrations in these sources are strongly influenced by the collection strategy. Biological oxygen demand (BOD) quantifies the amount of the dissolved oxygen required to biologically oxidize the organic contaminants; therefore, the larger the BOD value, the larger the organic contaminant concentration. Nitrogen-species, including NO$_3^-$, NO$_2^-$, and NH$_4^+$, and phosphates (PO$_4^{3-}$) were also considered. Whereas, nitrogen contaminants dominate in nuclear wastes (159,000 mg/L total nitrogen species), ion-exchange brines (5,270 mg/L), and power production processes (300 mg/L), organic species overshadow nutrient contaminants in municipal wastewater effluents and oil/gas processes. The concentrations of all three contaminants are comparable for effluents from manufacturing processes. In many waste streams, PO$_4^{3-}$ contamination is comparable to the nitrogen-contamination, which indicates the potential for phosphorous-recovery from these sources. For reference, the U.S. Environmental Protection Agency (EPA) established nitrogen-contaminant levels for drinking water are 44.3 mg-NO$_3^-$/L and 3.3 mg-NO$_2^-$/L.
More than 80% of all nitrogen-contaminants are in the form of NO$_3^-$ in all point sources except for oil/gas processes, where the NH$_4^+$ species predominates. Therefore, tertiary processes targeting nitrogen recovery could be valuable in pre-treated wastewaters from these sources. Furthermore, the source-dependent fluctuation in the NO$_3^-$ concentration establishes a need to quantify the impacts of this variation on the predicted process efficiencies and the removal/recovery rates.

### 4.2 Solar-to-Chemical Efficiencies and Nitrogen Removal/Recovery Rates

Figure 4 presents the equivalent-circuit model predictions for the solar energy conversion efficiencies (Eq. (14)) for NH$_3$ and N$_2$O production as a function of the semiconductor band gaps and electrocatalytic parameters. A bulk NO$_3^-$ concentration of 100 mM, which is approximately the average of the NO$_3^-$ concentration in the point-source effluents in Figure 3, was used in these
Figure 4: (a) Solar-to-chemical energy conversion efficiencies, \( \eta_{\text{solar-to-chemical}} \), for water oxidation and \( \text{NO}_3^- \) reduction to \( \text{NH}_3 \) (green) and \( \text{N}_2\text{O} \) (purple) with \( \text{RuO}_2 \), Cu (pH 14) and \( \text{IrO}_2 \), Sn-Pt (pH 1) catalysts for the OER and the NO3RR, respectively. Solar-to-hydrogen efficiency in the inset was computed for \( \text{RuO}_2 \) (OER) and Pt (HER) catalysts at pH=1; maximum solar-to-H\(_2\) efficiency is represented as a star\(^{38} \). The thick solid lines and the thin solid lines represent efficiencies with state-of-the-art and ideal nitrate reduction catalysts. Total kinetic overpotential, \( \eta_{\text{tot}} \), and the split between the oxidation (OER) overpotential, \( \eta_{\text{OER}} \), (dark shaded area) and the NO3RR overpotential, \( \eta_{\text{NO3RR}} \), (light shaded area) is shown for (b) NH\(_3\) (green) and (c) N\(_2\)O (purple). Standard state potential from Eq. (3) was used and a 100 mM NO\(_3^-\) species concentration was modeled; \( E_{\text{NO3RR}}^0 = 0.835 \text{ V vs NHE} \).

Calculations, and selective OER and NO3RR was modeled to estimate the upper limits for the solar energy conversion efficiencies. Irrespective of the catalytic parameters modeled, the solar-to-chemical efficiency initially increases with an increase in the semiconductor band gap until an optimum point, after which, the efficiency decreases. The optimum arises because of the tradeoffs between the increased light absorption for the smaller band gaps and the decreased radiative recombination losses for the larger band gaps. For state-of-the-art catalysts, peak solar-to-chemical
efficiencies are 10.1% and 7.3%, corresponding to peak nitrogen removal/recovery rates of 395.3 g N m⁻² day⁻¹ and 260.3 g N m⁻² day⁻¹, for N₂O and NH₃ formation respectively. The trends for the nitrogen removal/recovery rates are not shown in Figure 4 because they exactly match with the trends obtained for the solar-to-chemical efficiencies. The higher efficiencies and recovery-rates for the production of N₂O relative to NH₃ is due to the more effective catalysis for the NO₃RR with the Sn-Pt catalyst as compared to Cu. Therefore, at peak efficiencies, relatively smaller kinetic overpotentials resulted for N₂O as compared to NH₃—412 mV v/s 689 mV for the NO₃RR (Figure 4 (b) and (c)). Ideal efficiency plots were obtained by imposing rapid kinetics for the NO₃RR, i.e. \( \eta_{\text{red}} = 0 \), with state-of-the-art OER catalysts. The optimal solar-to-chemical efficiencies for the ideal case more than double, from 7.3% to 17%, for NH₃ and increase from 10.1% to 16.3% for N₂O, as compared to the state-of-the-art NO₃RR catalysts. The solar-to-chemical efficiency for N₂O formation is relatively less sensitive to the kinetic parameters modeled for NO₃RR, as opposed to NH₃ formation, because the OER overpotentials dominate the potential losses in the former. This dramatic boost in overall performance, achieved by eliminating the nitrate-reduction kinetic overpotential, indicates that effective nitrate reduction electrocatalysts can significantly boost the efficiencies for any light-absorber and that the performance predictions are highly sensitive to the catalytic parameters modeled. To place these efficiencies in context, Figure 4 also depicts the maximum solar-to-hydrogen conversion efficiency of 18% for a photoelectrochemical water splitting device with a single light-absorber (band gap of 1.96 eV) and with state-of-the-art OER and HER catalysts. The optimal efficiencies for the two processes are comparable when ideal/rapid NO₃RR reduction kinetics were assumed because the kinetic overpotentials for the state-of-the-art HER catalysts are much smaller than that for the NO₃RR catalysts. With state-of-the-art catalysts, the theoretical limits for the peak nitrogen-removal rates are comparable to the
maximum removal rates, of 520 gN m² day⁻¹, reported in (bio)electrochemical flow/continuous reactors for ammonia recovery⁶³.

Figure 5 depicts the effect of varying the bulk NO₃⁻ concentration, \(c_{\text{NO}_3,\text{bulk}}\), on the solar-to-chemical efficiency and the rate of nitrogen removal/recovery, while assuming selective NO3RR catalysis to form NH₃ (Figure 5(a) and (c)) or N₂O (Figure 5(b) and (d)). The bulk concentration of NO₃⁻ was varied from 0.1 mM to 1000 mM, representing the order-of-magnitude variation in the NO₃⁻ concentrations corresponding to the EPA limit in drinking water to the presence of NO₃⁻ in concentrated wastewater sources such as ion-exchange brines (Figure 3). Overall, for any concentration modeled, converting the NO₃⁻ to N₂O, as compared to NH₃, results in larger efficiencies and nitrogen removal/recovery rates (12.01% v/s 9.68% at 1000 mM) because of the more effective NO3RR catalysis in the former with Sn-Pt catalysts (Figure 4). There is a logarithmic scaling in the maximum efficiencies and the nitrogen removal/recovery rates with the NO₃⁻ concentration, because of the larger driving force and therefore lower kinetic overpotentials for the electron-transfer reactions (Eq.(12)).

For \(c_{\text{NO}_3,\text{bulk}} = 10, 100 \text{ and } 1000 \text{ mM}\), the transport of NO₃⁻ from the bulk solution to the electrode surface does not impact the operating current densities at any band gap of the semiconductor as the mass-transfer limited current density (Eq. (10)) for the NO3RR is much larger than the short-circuit density of the light-absorber. For these concentrations, when the band gaps are smaller than the optimal value, the concentration-dependent NO3RR kinetics limits both the efficiency and nitrogen removal/recovery rates. For the same range of NO₃⁻ concentration, when the band gaps are larger than 2 eV, the performance is insensitive to changes in the concentration because light-absorption in the semiconductor limits the performance. However, for
the two smaller concentrations, $c_{\text{NO}_3^{\text{bulk}}} = 0.1 \text{ mM}$ and 1 mM, there is a mass-transfer limited operational regime in addition to the kinetics and light-absorption limited performance. In this regime, there is little-to-no effect of the band gap on the performance, resulting in the plateau.
region observed in Figure 5(a) and (b). In these conditions, the operating current density of the device (Eq. (4)), is predominantly limited by the rate of diffusion of the reacting NO$_3^-$ species from the bulk electrolyte to the electrocatalyst surface. For NH$_3$ production, mass-transfer limited efficiencies of 1.62% and 0.16% are predicted for the band gaps of 2.15 – 2.75 eV and 1.65 – 2.75 eV, with $c_{\text{NO}_3^-,\text{bulk}} = 1 \text{ mM}$ and 0.1 mM respectively. Therefore, the bulk NO$_3^-$ concentration in the waste steam not only has an impact the maximum attainable efficiencies and the nitrogen recovery rates, but also affects how sensitive the performance is to the light-absorber band gaps.

Figure 6 reveals the extent to which the competing reactions influences the solar-to-chemical efficiencies. The green and the purple shaded areas (for NH$_3$ and N$_2$O respectively) represent the absolute change in efficiency, from assuming selective catalysis to when the worst-case was modeled for the competing reactions. Four discrete band gaps were selected to represent realistic semiconductor materials for the light absorbers—Si (1 eV), MoS$_2$ (1.75 eV), BiVO$_4$ (2.5 eV), and TiO$_2$ (3.1 eV). Three bulk NO$_3^-$ concentrations of 1000, 10, and 1 mM were selected to highlight the trends. Consider the results for the NO$_3^-$-to-NH$_3$ transformation (Figure 6(a)). For all bandgaps, competing reactions results in lower solar-to-chemical efficiencies and nitrogen removal/recovery rates. The peak efficiencies, from Figure 5 are reduced by 9% and 63% for 1000 mM and 1 mM NO$_3^-$ respectively. For any band gap, the relative decrease in the efficiency becomes larger when the bulk concentration of NO$_3^-$ becomes smaller (Figure S1 in ESI). This outcome is due to the increase in the NO3RR mass-transfer overpotential with a decrease in the NO$_3^-$ concentration, which in turn increases the driving force for the competing reactions. For the intermediate band gap materials—MoS$_2$ (1.75 eV) and BiVO$_4$ (2.5 eV) – ORR occurs at the mass-transfer limited current density of $\sim 21 \text{ A m}^{-2}$ for all NO$_3^-$ concentrations (blue circles in Figure 6 (b)). However, the rate of competing HER increases when the NO$_3^-$ concentration decreases.
Figure 6: Solar-to-chemical efficiency for (a) NH₃ production and (c) N₂O production when competing HER and ORR reactions are implemented at the cathode with worst-case kinetic parameter values (Table 2). (b,d) To further illustrate the driving forces for the competing reactions, the current-voltage behavior for the diode (black) assuming BiVO₄ with a band gap of 2.5 eV and the parallel and competing electrochemical reactions at the cathode. Open symbols on the current-voltage plot represent models that assumed selective reactions whereas the filled symbols include the competing reactions. The operating point, $f_{\text{op}}$ and $V_{\text{op}}$, is shown on the diode curve (black circles); the cathode potential and current densities for (b) NH₃ production (green) or (d) N₂O production (purple); HER (yellow); and ORR (blue).
below 10 mM (yellow circles in Figure 6(b)). For $c_{\text{NO}_3,\text{bulk}} > 1$ mM, mass-transfer limited H$_2$ oxidation occurs instead of H$_2$ evolution because the cathode potential is larger than the equilibrium potential of H$^+/\text{H}_2$, $V_{\text{cathode}} > E_{\text{eq,HER}} = 0.19$ V v/s RHE, assuming a head-space with 0.5 ppm H$_2$. For a bulk NO$_3^-$ concentration of 1 mM and a band gap of 2.5 eV, while the NO3RR is mass-transfer limited when selective NO3RR was modeled (open green circles in Figure 6(b)), this limitation ceases to exist when competing reactions were taken into account at the cathode (filled green circles in Figure 6(b)). This trend is also evident in the shift of the operating potential and current densities of the diode (open versus closed black circles) on the diode curve in Figure 6(b). For both Si (1.1 eV) and TiO$_2$ (3.1 eV), the baseline efficiencies without the competing reactions are small due to the lack of driving potential at the cathode for the NO3RR in Si and because of the limited visible light absorption for TiO$_2$. In both these instances, mass-transfer limited ORR predominates at the cathode as compared to the NO3RR; H$_2$ oxidation occurs at negligibly small, mass-transfer limited rates of $3.87 \times 10^{-5}$ A m$^{-2}$, for all NO$_3^-$ concentrations in the bulk.

For the NO$_3^-$-to-N$_2$O transformation (Figure 6(c)), overall trends are largely similar to what was previously discussed for the NO$_3^-$-to-NH$_3$ transformation. A subtle difference occurs with respect to the effects of competing HER for the low NO$_3^-$ concentrations ($\leq 1$ mM). While HER becomes more significant at these NO$_3^-$ concentrations for NH$_3$ production, it is not the case for N$_2$O formation because of the lower kinetic potential losses. Therefore, the current onset occurs at a much lower potential on the Sn-Pt catalyst for N$_2$O formation as compared to the Cu catalyst for NH$_3$ production. For example, with the BiVO$_4$ light-absorber with a 2.5 eV bandgap, Figure 6(d) reveals that the NO3RR is mass-transfer limited for, both, with and without competing reactions, and therefore the efficiency does not change (Figure 6(c)). The conversion of NO$_3^-$ to N$_2$O benefits
from more efficient catalytic parameters modeled as compared to NH₃, especially at the low NO₃⁻ concentrations.

Overall, even with large driving forces for the competing reactions established by the worst-case parameters modeled herein, these results indicate that the competing reactions do not significantly influence the performance (at most 10% relative change in efficiencies and the nitrogen removal/recovery rates) when the NO₃⁻ concentrations are large (≥ 100 mM) and with optimally selected band gaps. In these cases, the most dominant competing reaction at the cathode is the ORR, which is mass-transfer-limited to current-densities less than 21 A m⁻², which is at least five times lesser than the NO₃RR current densities.

4.3 Comparison with state-of-the-art nitrogen-removal technologies

We compared the proposed device with two tertiary technologies that are currently used for nitrogen removal and recovery—(1) electrochemical ammonia stripping⁶³, and (2) the Sharon-Anammox process that removes NH₃/NH₄⁺ contaminants as N₂⁶¹,⁶². These three pathways were compared on the basis of the nitrogen-removal rates and the mass-specific energy intensity (Table 3). For this comparison, we assumed bulk NO₃⁻ concentration of 100 mM, state-of-the-art catalysts with perfect selectivity for the NO₃RR for NH₃/NH₄⁺ production; Figure 6 indicates that the competing reactions do not substantially alter the performance for the 100 mM case. More information about these processes are provided in the ESI (Section 3).

For the nitrogen-removal rates, the proposed photoelectrochemical approach achieves nitrogen removal rates comparable to those reported for the electrochemical ammonia-stripping reactors – 272.2 and 411.3 gN m⁻² day⁻¹ for NH₃ and N₂O production respectively with state-of-the-art catalysts and 100 mM bulk NO₃⁻ concentration. The Sharon-Anammox is a batch process and thus limited to lower rates of nitrogen removal as compared to the flow reactors, roughly
10 \text{ g}_N \text{ m}^{-2} \text{ day}^{-1} \) (Section 3 in ESI for calculation details). Therefore, the mass-specific energy intensities were compared at this fixed nitrogen removal rate of 10 \text{ g}_N \text{ m}^{-2} \text{ day}^{-1}. About 10–16 \text{ MJ kg}_N^{-1} is required by the Sharon-Anammox process, including aeration, pumping and other parasitic power inputs at the plant-scale\textsuperscript{61,62}. A specific energy intensity of ~2.4 \text{ MJ kg}_N^{-1} is estimated, without any consideration of parasitic energy requirements, for the electrochemical ammonia stripping reactor\textsuperscript{63}. In comparison, at equivalent nitrogen-removal rates, the energy intensity for the photoelectrochemical approach proposed in this work is 8 \text{ MJ kg}_N^{-1}, out of which 2.9 \text{ MJ kg}_N^{-1} is required for the \text{NO}_3^-–to–\text{NH}_4^+ transformation, 2.6 \text{ MJ kg}_N^{-1} is estimated for pumping in a flow reactor\textsuperscript{98}, and an energy requirement of 2.4 \text{ MJ kg}_N^{-1} was additionally included to recover the \text{NH}_3/\text{NH}_4^+ formed via electrochemical ammonia stripping. Therefore, the proposed approach has the potential to competitive with one of the most energy-efficient nitrogen-removal technologies with the added dual benefits of harnessing sunlight to treat and remove reactive-nitrogen (\text{NO}_3^-) contaminants while also recovering nutrients as \text{NH}_3/\text{NH}_4^+ (or \text{N}_2\text{O}).

Table 3: Nitrogen-removal rates and mass-specific energy intensity comparisons for the Sharon-Annamox, electrochemical flow reactor for ammonia stripping and the photoelectrochemical approach discussed in this work.

<table>
<thead>
<tr>
<th>Metrics (Units)</th>
<th>Sharon-Annamox</th>
<th>Electrochemical flow reactor for ammonia stripping</th>
<th>Photoelectrochemical device for nitrate-to-ammonia conversion (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen-removal rates (\text{g}_N \text{ m}^{-2} \text{ day}^{-1})</td>
<td>10</td>
<td>384</td>
<td>272.2</td>
</tr>
<tr>
<td>Mass-specific energy intensity (\text{MJ kg}_N^{-1}) for nitrogen removal at a rate of 10 \text{ g}_N \text{ m}^{-2} \text{ day}^{-1}</td>
<td>10-16</td>
<td>2.4</td>
<td>8</td>
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</table>

5. Conclusions

In summary, we propose and analyze the performance of a solar-powered wastewater nitrate treatment process that couples water oxidation with nitrate reduction to produce value-
added chemicals such as NH$_4^+$/NH$_3$ and N$_2$O. A numerical model was developed to predict the influences of material- and operational- parameters on solar-to-chemical efficiencies and the nitrogen removal/recovery rates. Important modeling innovations were introduced to quantify the influences of reacting species concentrations in the bulk solution and the competing hydrogen evolution and oxygen reduction reactions on the performance. Results reveal that the overall performance of the proposed device is influenced by the combined effects of light absorption in the semiconductor, which was modeled as a function of the band gap; electrocatalytic parameters including the exchange current densities and charge-transfer coefficients for the water oxidation and nitrate reduction reactions; and the species concentrations, which impacted the rates of diffusion of species across the concentration boundary layer.

For a bulk NO$_3^-$ concentration of 100 mM, model results predict peak solar-to-chemical efficiencies of 7% and 10%, and nitrogen removal/recovery rates of 260 gN m$^{-2}$ day$^{-1}$ and 395 gN m$^{-2}$ day$^{-1}$, for NH$_3$ and N$_2$O production with Cu and Sn-Pt catalysts respectively; optimal light-absorber band gaps are 1.89 eV and 1.58 eV respectively. The reacting NO$_3^-$ species concentration impacts the reaction kinetics by influencing the concentration-dependent exchange-current densities and the mass-transfer limited nitrate reduction current densities. For NO$_3^-$ concentrations larger than or equal to 10 mM, efficiencies and the nitrogen removal/recovery rates are limited by the nitrate reduction kinetics or the light-absorber current-voltage behavior. However, for the smaller NO$_3^-$ concentrations, there is a mass-transfer limited operating regime, wherein the efficiencies and the nitrogen removal/recovery rates are unaffected by changes in the light-absorber band gap and the electrocatalytic parameters. In this regime, the operating current densities are only limited by the rate of diffusion of the NO$_3^-$ ions, from the bulk to the surface of the electrocatalyst across a 10-µm thick concentration boundary layer. Competing hydrogen
evolution and oxygen reduction reactions were modeled with worst-case parameters deduced from kinetics for these reactions on a Pt-catalyst. For large concentrations ($\geq 100$ mM) of nitrates and optimally selected light-absorber band gaps, oxygen reduction is the more dominant competing reaction and is mass-transfer limited. Therefore, the peak efficiencies and the nitrogen removal/recovery rates are at most reduced by 11%. The driving force for the hydrogen evolution reaction increases for the smaller NO$_3^-$ concentrations and for increasing light-absorber band gaps.

Model predictions were used to identify light-absorber materials, based on the calculated effects of their band gaps, for NH$_3$ and N$_2$O production. For example, MoS$_2$ with a band gap of 1.75 eV can yield high efficiencies and nitrogen removal rates for NO$_3^-$-to-NH$_3$ conversion, when NO$_3^-$ concentrations are larger than 10mM. When the concentration becomes smaller, even with a larger band gap light-absorber, such as BiVO$_4$ (2.5 eV), the efficiency remains unaffected. Theoretical predictions for the performance of the proposed photoelectrochemical device in attractive when compared with the state-of-the-art nitrogen removal technologies. A comparative analysis revealed that the nitrogen removal rate and the energy intensity of nitrogen-removal are competitive with reported estimates for electrochemical ammonia stripping and the Sharon-Anammox process.

On the whole, theoretical analyses in this study indicate that transforming wastewater nitrates to value-added chemicals, including NH$_3$ and N$_2$O, by utilizing sunlight can be a promising new approach to achieve resource recovery in tertiary wastewater treatment technologies. Future investigations will focus on experimental measurements to further build on this work and to assess the performance of the catalysts and semiconductor materials identified in this work.
Acknowledgments

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References


75. Chang, C. & Wen, T. Kinetics of Oxygen Reduction at IrO2-Coated Titanium Electrode in
2. Sheng, W., Gasteiger, H. A. & Shao-Horn, Y. Hydrogen Oxidation and Evolution
3. Sheng, W., Myint, M., Chen, J. G. & Yan, Y. Correlating the hydrogen evolution reaction
   activity in alkaline electrolytes with the hydrogen binding energy on monometallic
5. Dong, Q., Santhanagopalan, S. & White, R. E. Simulation of the Oxygen Reduction
   Reaction at an RDE in 0.5 M H2SO4 Including an Adsorption Mechanism. **154**, (2007).
8. Reyter, D., Chamoulaud, G., Bélanger, D. & Roué, L. Electrocatalytic reduction of nitrate
9. Mattarozzi, L. *et al.* Electrochemical reduction of nitrate and nitrite in alkaline media at
12. Hirakawa, H., Hashimoto, M., Shiraishi, Y. & Hirai, T. Photocatalytic Conversion of
    Nitrogen to Ammonia with Water on Surface Oxygen Vacancies of Titanium Dioxide. *J.
13. Suryanto, B. H. R. *et al.* Challenges and prospects in the catalysis of electroreduction of
    and science. (2003).
    and Health Advisories Tables. (2018).
    Standards for the Oil and Gas Extraction Point Source Category*. United States
    Environmental Protection Agency vol. EPA-820-R- (2016).
17. U.S. Environmental Protection Agency & US EPA. Development document for final
    effluent limitations guidelines and standards for the iron and steel manufacturing point
    source category. 1062 (2002).
18. U.S. Environmental Protection Agency. Industrial Wastewater Treatment Technologies
    Database.
    Electrochemical Reactor Model for the Destruction of Nitrate and Nitrite in Alkaline
20. Moreno, C., Farahbakhshazad, N. & Morrison, G. M. Ammonia removal from oil refinery

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Electronic Supplementary Information

Harnessing Photoelectrochemistry for Wastewater Nitrate Treatment Coupled with Resource Recovery

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# 1. Nomenclature

### Symbols

- $a$ activity of modeled aqueous/dissolved species, unitless
  
  with $a_{O/R} = \frac{c_{O/R}}{c_{O/R,ref}}$

- $c$ speed of light, $3.0 \times 10^8$ m s$^{-1}$

- $C$ concentration of modeled species, mol m$^{-3}$

- $D$ diffusion coefficient of modeled species, m$^2$ s$^{-1}$

- $E^0$ standard electrochemical potential, V vs NHE

- $E_g$ band gap of the semiconductor material, eV

- $E_{eq}$ Nernst potential, V

- $E_N$ specific energy intensity, MJ kgN$^{-1}$

- $F$ Faraday’s constant, 96485 C mol$^{-1}$

- $\Delta g^0$ standard state free energy change associated with a reaction, kJ mol$^{-1}$

- $h$ Planck constant, $6.626 \times 10^{-34}$ J s

- $j$ current density, A m$^{-2}$

- $j_0$ exchange current density, A m$^{-2}$

- $k_B$ Boltzmann constant, $1.38 \times 10^{-23}$ J K$^{-1}$

- $m_N$ molar mass of nitrogen, 14 g N mol$^{-1}$ or 0.014 kg N mol$^{-1}$

- $n_d$ ideality factor of the diode, here assumed to be 1

- $n_e$ number of electrons exchanged during reaction

- $R_N$ nitrogen-removal rate, gN m$^{-2}$ day$^{-1}$

- $q_e$ elementary charge, $1.6021 \times 10^{-19}$ C

- $\dot{r}$ molar flux, mol m$^{-2}$ s$^{-1}$

- $R$ gas constant, 8.314 J K$^{-1}$ mol$^{-1}$

- $T$ ambient temperature, 298.15 K (here, also the diode temperature)

- $t_{day}$ number of seconds in a day, 86400 s day$^{-1}$

- $V$ potential, V

### Greek

- $\alpha$ charge-transfer coefficient

- $\delta_{BL}$ boundary-layer thickness, µm

- $\eta$ kinetic overpotential, mV

- $\eta_{solar\text{-to}\text{-chemical}}$ solar-to-chemical efficiency, %

- $\nu$ photon frequency, s$^{-1}$

- $\nu$ stoichiometric coefficient for modeled reactions

- $\phi$ frequency-dependent photon flux, s$^{-1}$ m$^{-2}$

### Subscripts

- $a$ pertinent to the anode

- $\text{bulk}$ pertinent to species concentration

- $c$ pertinent to the cathode

- $g$ indicating the min. frequency of photons that can be absorbed by the diode

- $i$ pertinent to the reaction modeled

- $k$ pertinent to the kinetic overpotential

- $l$ pertinent to the limiting current density

- $mt$ pertinent to the mass-transport overpotential
O pertinent to the oxidized species
op pertinent to the operating current density and potential of the device
R pertinent to the reduced species
ref pertinent to the reference value from the literature
rr pertinent to the radiation recombination current density
sc pertinent to the short-circuit current density
solar pertinent to the incident solar spectrum
tot total

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2. Solar-to-Chemical Efficiencies and Nitrogen Removal/Recovery Rates

Figure S1 shows the relative difference (RE) for the solar-to-chemical efficiency was calculated by comparing the efficiencies with, \( \eta_{\text{solar-to-chemical,comp}} \), and without, \( \eta_{\text{solar-to-chemical,no comp}} \), competing reactions as function of the bulk NO\(_3^–\) concentration. Both HER and ORR were implemented with “worst-case” kinetic parameters. An increase in this relative difference corresponds to an increase in the effect of the competing reactions; a value of 100% implies that the efficiency value with competing reactions approached 0. On Figure S1(a), the relative difference decreases with increasing concentration for all band gaps, with the largest values overall reached by TiO\(_2\) and Si. For the formation of N\(_2\)O, on Figure 1(b), the smaller concentrations show less of an effect due to the competing reactions, which follows from the mass-transport limited behavior of the NO3RR shown on Figure 6.

\[
RE(\%) = \frac{\eta_{\text{solar-to-chemical,no comp}} - \eta_{\text{solar-to-chemical,comp}}}{\eta_{\text{solar-to-chemical,no comp}}} \tag{S1}
\]

Figure S1: Relative decrease (\%) as a function of NO\(_3^–\) concentration for Si (red), MoS\(_2\) (orange), BiVO\(_4\) (yellow) and TiO\(_2\) (purple) as discussed in Figure 6 for the (a) NO\(_3^–\)-to-NH\(_3\) transformation and (b) NO\(_3^–\)-to-N\(_2\)O transformation
3. Comparison with state-of-the-art nitrogen-removal technologies

The ammonia stripping reactor recovers NH$_3$/NH$_4^+$ nutrients that are present in the solution in an electrochemical flow cell by applying an electric field$^1$. This approach offers the advantages of high nitrogen-recovery rates, up to 384 gN m$^{-2}$ day$^{-1}$, because of improved mass-transport in flow reactors$^3$. However, it relies on the presence of NH$_3$/NH$_4^+$ in the waste stream, unlike our device that transforms the NO$_3$- to NH$_3$ or N$_2$O already.

The Sharon-Anammox process is an energy-efficient, biological pathway to transform reactive-nitrogen contaminants present in the form of NH$_3$/NH$_4^+$ to N$_2$$^2$. However, with this approach the nutrients in wastewater are not recovered but lost as N$_2$. Because this process is typically carried out in batch-reactors, volumetric nitrogen-removal rates of up to 2 kgN m$^{-3}$ day$^{-1}$ have been reported$^{3,4}$. To translate the volumetric rate to an aerial rate, a biofilm/membrane specific surface area of ~200 m$^{-2}$ m$^{-3}$ was assumed$^5$, which results in an areal rate of approximately 10 gN m$^{-2}$ day$^{-1}$.

References:
Harnessing Photoelectrochemistry for Wastewater Nitrate ... (0.95 MiB)  view on ChemRxiv  download file