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Rethinking nitrate reduction: redirecting electrochemical efforts from ammonia to nitrogen for realistic environmental impacts†

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The excessive use of nitrate in agriculture and industry poses a significant threat to human health and ecosystems. To effectively manage the nitrogen cycle (N-cycle) in nature and to deal with nitrate pollution in wastewater, various electrochemical approaches have been developed to convert nitrate into N-products. Recent research works have focused their efforts on electrochemical nitrate reduction (eNO₃R) to ammonia (NH₃) as “an alternative approach to the Haber–Bosch process” while reducing the environmental impacts. However, when considering challenges due to the low concentration of nitrate in wastes and difficulties in extracting as-synthesized NH₃ and comparing this scale with the scale of current NH₃ and nitrate production, such an eNO₃R to NH₃ approach at the largest possible scale, even without examining its economic viability and overall environmental implications, will have an insignificant impact. Therefore, we recommend that rational implementation approaches for nitrate treatment should involve converting nitrate ions at low concentrations into nitrogen (N₂) gas or recycling them at high concentrations to produce other nitrate chemicals or fertilizers.

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Broader context

With the growing world population and increasing human activities, nitrate pollution in water bodies has caused severe health and environmental issues. To provide clean drinking water and balance the nitrogen cycle (N-cycle) in nature, numerous research efforts have focused on removing nitrate from wastewater using electrochemical approaches. Several recent studies have claimed that converting waste nitrate into ammonia (NH₃) with high catalytic performance provides an alternative approach to the Haber–Bosch process. Unfortunately, such a “waste-to-wealth” conversion will likely have insignificant impacts and should be considered an unnecessary distraction. To deliver realistic environmental impacts, our analysis deems that the low-concentration nitrate in wastewater should be directly converted into harmless N₂ gas through electrochemical reactions, and for the case of high concentrations, nitrate ions should be recycled and purified to generate nitrate chemicals or fertilizers.

Background

Ammonia (NH₃), as one of the most important chemicals, plays a vital role, particularly in the production of fertilizers for agriculture that feeds the world population.^{1–3} The global production of NH₃ reaches over 180 million tonnes (Mt) per year with a market value of ~US\$75 billion.^{4–6} This massive amount of NH₃ is produced through the conventional Haber–Bosch process, accounting for 1–2% of the world's energy demand and contributing to 1–1.5% of

annual anthropogenic CO₂ emissions.^{7,8} Around 75% of NH₃ is utilized in the agricultural sector for the production of fertilizers and synthesis of nitric acid (HNO₃), another critical industrial feedstock for manufacturing fertilizers.⁹ The remaining ~25% is employed in plastics, explosives, food and synthetic fibers manufacturing industries.¹⁰ In particular, almost 100% of nitric acid production relies on the energy-intensive Ostwald process: NH₃ oxidation at high temperatures (600–900 °C) and pressure (410–1000 kPa).^{11,12} The global production of nitric acid totals approximately 60 Mt per year, with a market value of around US\$30 billion, of which about 70% is exploited to produce ammonium nitrate (NH₄NO₃) as a modern agricultural fertilizer.^{11,13} Moreover, about 13% of nitric acid is used for organic oxidation reactions, which also constitute a vital intermediate for organic nitrations. The remaining nitric acid is consumed for the synthesis of other materials and chemical processes. This signifies the essential roles of large nitric acid production and its utilization in fertilizer

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Table 1 Various types of nitrate-polluted wastewater and criteria for drinking water

Type of wastewater	pH	N-species	Nitrate concentration (N-mg L ⁻¹)
Polluted groundwater ¹⁹	Unknown	NO ₃ ⁻ , NO ₂ ⁻ , NH ₄ ⁺	12–18
Textile wastewater ²⁰	7	NO ₃ ⁻	104
Industrial wastewater ²¹	7.9	NO ₃ ⁻ , NH ₄ ⁺	582.4
Low-level nuclear wastewater ²²	Alkaline	NO ₃ ⁻ , NO ₂ ⁻ , Ru(NO(NO ₂) ₄ (OH)) ²⁻	27 300
Drinking water ¹⁸	6.5–8.5	NO ₃ ⁻ , NO ₂ ⁻ , NH ₄ ⁺	< 10

industries. Furthermore, the escalating global population and economic activities will continue to increase the demand for nitric acid production in the future. Its excessive use for agricultural purposes and the improper disposal of industrial wastes, however, can lead to health and environmental issues.

Nitrate contamination in drinking water (NO₃⁻ > 10 N-mg L⁻¹) mainly results from agricultural and industrial activities and has health impacts, such as causing methemoglobinemia, cancer, and thyroid problems.^{14–17} In addition, the rising NO₃⁻ concentration can disrupt the natural N-cycle by releasing reactive nitrogen species into the environment. Table 1 lists the concentrations of nitrate in various types of contaminated wastewater.¹⁶ Concerning public health, the World Health Organization (WHO) recommends maximum contaminant levels of 10, 0.03, and 0.4 N-mg L⁻¹, respectively, for NO₃⁻, NO₂⁻, and NH₄⁺ in drinking water.¹⁸

Electrochemical NO₃⁻ Reduction (eNO₃R) to NH₃

Impractical potential

To address nitrate pollution in wastewater and mitigate the natural N-cycle imbalance, a growing number of studies have been reported on the electrochemical NO₃⁻ reduction to NH₃ (Fig. 1), with strong catalytic performances achieved, including a current density as high as ~1 A cm⁻² and ~100% faradaic efficiencies.^{23–25} Some reports have even asserted that electrochemical NO₃⁻ reduction to NH₃ under ambient conditions utilizing nitrate wastes as feedstock could be an alternative to

the conventional Haber–Bosch process.^{26–29} Although significant progress has been made in the electrochemical conversion of NO₃⁻ to NH₃ in terms of current densities and faradaic efficiencies, the feasibility of large-scale NH₃ production remains highly questionable due to the insufficient concentration and low capacity of nitrates feedstock in real wastewater. Taking the widespread fertilizer ammonium nitrate as an example, about 17% of nitrate ions would leach to the groundwater as nitrate contaminants annually.³⁰ Even if those nitrate contaminants can be successfully converted to NH₃ with 100% selectivity using an electrochemical approach, the estimated amount of ammonia produced would only be about 2 Mt year⁻¹. Such a “waste-to-wealth” conversion approach is insignificant compared to the NH₃ production accomplished using the conventional Haber–Bosch process, even without considering the energy needs for NO₃⁻ collection and reduction, and NH₃ separation, purification, and compression, and a significant amount of the NH₃ produced would be oxidized for the nitric acid production.

Unintentional environmental challenges

In another area of research that focuses on adopting environmentally friendly approaches to address nitrate contaminants in wastewater, various technologies such as reverse osmosis, bacterial denitrification, and ion exchange are currently being employed on a commercial scale.³¹ However, those technologies are expensive and require harsh reaction conditions. In contrast, electrochemical reduction of nitrate to ammonia powered by renewable electricity would seem to be a more sustainable method for treating wastewater than existing commercial technologies,^{32,33} but, unfortunately, may not be economically viable despite the reported high selectivity and efficiency of NO₃⁻-to-NH₃ conversion due to the resulting low concentration of NH₃.³⁴ Moreover, any NH₃ not completely isolated would itself be a more serious contaminant than NO₃⁻ in wastewater.

Conclusion and outlook

In summary, electrochemical NO₃⁻ reduction to NH₃ may show some scientific merits, but when considering practical and industrial implementations, this process will likely play an insignificant role in either NO₃⁻ contaminants removal or NH₃ production.^{35,36} When dealing with NO₃⁻ contaminants in real wastewater, NO₃⁻ should not be converted to NH₃ at any concentration range: at high concentrations, NO₃⁻ is a more valuable feedstock (as it has to be produced from NH₃), with the

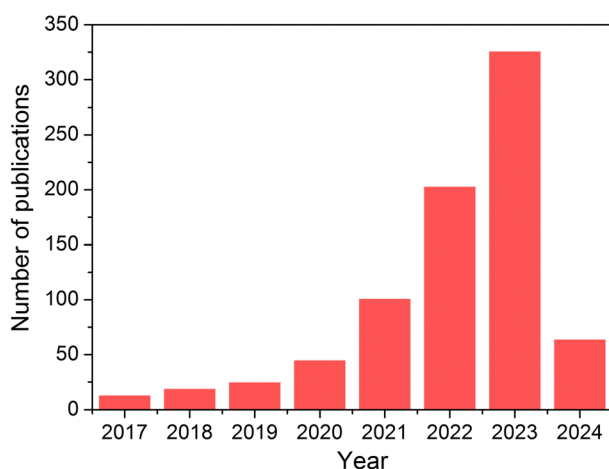


Fig. 1 Number of publications per year on “electrochemical nitrate reduction to ammonia.” Source: Web of Science on Mar. 29, 2024.



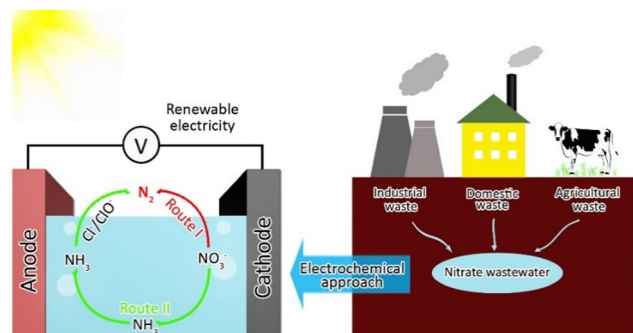
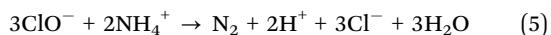
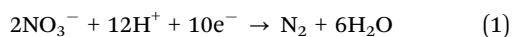


Fig. 2 Schematic diagram of electrochemical reduction of nitrate to nitrogen gas for wastewater denitrification.

production costs and energy consumption of NH_3 using the electrochemical NO_3^- reduction process being 2.04 times higher than those of the Haber–Bosch process (the detailed calculation is provided in Table S1, ESI†);³⁷ at low concentrations, NH_3 produced from reducing NO_3^- becomes a more serious contaminant. For a more feasible and meaningful N-cycle to address nitrate pollution issues, following directions are recommended.

I. NO_3^- reduction to N_2

In wastewater denitrification, instead of focusing on converting NO_3^- to NH_3 , directly converting low-concentration nitrate ($10\text{--}1\,000\text{ N-mg L}^{-1}$) into harmless N_2 gas through electrocatalysis powered by renewable electricity would be more practical (Route I, Fig. 2 and eqn (1)).^{38,39} Alternatively, NO_3^- can be converted into NH_3 first on the cathode side, followed by the oxidation of NH_3 at the anode side to produce N_2 with the assistance of chloride ions in wastewater (Route II, Fig. 2, and eqn (2)–(5)),^{40,41} and in this way, risks induced by the potential byproducts of the e NO_3R process, such as ClO_3^- , trichloromethane, bromodichloromethane, or dibromochloromethane, are mitigated or avoided.^{42,43} Such a route can also be applied for removing $\text{NH}_3/\text{NH}_4^+$ from wastewater.



II. NO_3^- recovery

In the case of wastewater containing nitrate at high concentrations (above $1\,000\text{ N-mg L}^{-1}$), a more pragmatic approach can be recycling and purifying nitrate salts to produce NO_3^- chemicals or fertilizers rather than converting them into NH_3 .^{44,45}

III. Coupling with CO_2 reduction for value-added N-fertilizers

Value-added N-fertilizers might be generated or co-produced during the removal of nitrate from wastewater. For instance,

urea can be produced by coupling NO_3^- reduction with CO_2 reduction.^{46,47} An electrochemical approach has been recently reported for recovering $\text{NH}_3/\text{NH}_4^+$ from manure wastewater and co-producing NH_4^+ -rich fertilizer.⁴⁸ These technologies, however, are still in their early stages. Investigations of larger-scale implementation, improvement of energy efficiencies, and economic viability optimization will be needed to create meaningful impacts.

Conflicts of interest

There are no conflicts to declare.

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