Subject strapline: Resource recovery

Enroute to circular nitrogen economy

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Standfirst:

Recovering ammonia from industrial wastewater via nitrate-to-ammonia reduction for a more sustainable nitrogen cycle faces challenges due to complex wastewater matrices and suboptimal reactor design. Now, research presents a membrane-free electrolysis system for efficient and stable ammonia recovery from actual wastewater.

Nitrogen is a vital nutrient and essential element, especially in the form of ammonia, which is widely used in agriculture and industries. However, the current anthropogenic nitrogen cycle is unsustainable. The energy-intensive Haber-Bosch process, which synthesizes ammonia, consumes approximately 1-2% of the world's energy. After use, a significant amount of nitrogen ends up as nitrate (NO_3^-) in wastewater, posing a substantial threat to ecological balance and human health[1]. One potential solution is to recover nitrogen nutrients while removing NO_3^- pollutants from contaminated water[1]. The electrocatalytic conversion of NO_3^- to ammonia is an efficient and sustainable method that could benefit the future global nitrogen cycle[2]. However, co-existing pollutants in wastewater impede the practical industrial application of conventional membrane-based electrochemical reactors[3]. Writing in *Nature Sustainability*, Zhang and colleagues demonstrate a long-lasting, corrosion-resistant membrane-free electrolysis system, consisting of a 3D-printed electrode and a flow-through electrochemical cell, for recovering ammonia from NO_3^- rich wastewater[4].

Industrial activities, such as chemical synthesis, military operations, and fertilizer manufacturing, generate NO_3^- rich wastewater. These wastewaters often have high concentrations of NO_3^- and are classified as hazardous wastes that require solidification before disposal in landfills. The excessive NO_3^- loading not only increases treatment costs but also poses a risk of groundwater contamination through potential leakage[5]. The Electrocatalytic Nitrate Reduction Reaction (ENRR) offers a sustainable solution for converting NO_3^- to ammonia (NH_3), providing an effective method for treating these NO_3^- rich wastewaters (Fig. 1). By recovering NH_3 through ENRR, wastewater treatment costs can be substantially reduced, while also meeting global demand for NH_3 without the energy consumption and carbon emissions associated with the Haber-Bosch process[6].

Conventional ENRR systems commonly utilize proton exchange membranes (PEMs) to prevent NH_3 from re-oxidizing at the anode. However, these systems are inefficient and costly when treating NO_3^- wastewaters with high salinity, organic impurities, dissolved solids, and alkalinity. Limited mass transfer in conventional reactors results in reduced ENRR selectivity in later reaction stages, increasing energy consumption for NO_3^- to NH_3 conversion[7]. Another challenge is the high sensitivity of PEMs to organic impurities and dissolved solids, resulting in a lifespan of less than 200 hours and a notable rise in cell voltage. Furthermore, despite the development of various electrode materials, the corrosion resistance and stability of the electrodes remain significant issues[8]. To be viable for practical industrial use, ENRR systems must exhibit long-term operational stability and enhanced NO_3^- to NH_3 conversion efficiency[9].

To address these challenges, Zhang et al. utilized 3D printing technology to fabricate CuNi porous alloy electrodes. Copper and its alloys were chosen for electrode development due to their ability to reduce the energy barrier for the rate-limiting step in NH_3 generation[10,11]. The additive manufacturing process yielded a Cu-Ni metallic glass layer with a thickness of less than 5.0 nm through rapid cooling at the microscale. The electrode demonstrated excellent corrosion resistance during stability testing. The researchers further designed a membrane-free Electrochemical NO_3^- Conversion Synchronized with NH_3 Recovery (ECSN) system, which effectively prevented unwanted anode side reactions by integrating a flow-through cell and a photo-assisted stripping unit. The innovative system and electrode designs enable high electrochemical activity and corrosion resistance, leading to outstanding performance at high current densities. This ECSN system could operate continuously for 1000 hours at an industrial current density when treating actual wastewater from electroplating and photovoltaic enterprises, recovering approximately 70% of NH_3-N.

The results indicate that the ECSN system effectively addresses the challenges encountered by conventional electrochemical reactors when treating complex wastewater compositions with high salinity. The integration of the flow cell and photo-stripping unit is the key to an efficient recovery of NH_3 while preventing NH_3 loss from anode-side reactions. Moreover, in comparison to the conventional evaporation-crystallization-solidification-landfill (ECSL) method, the ECSN system reduces treatment costs by up to 47.0% and decreases environmental impacts related to global warming potential, terrestrial ecotoxicity, and human non-carcinogenic toxicity by 60.4%, 84.0%, and 49.1%, respectively.

Overall, the ECSN system introduced by Zhang et al. paves the way to a sustainable anthropogenic nitrogen cycle and, ultimately, a circular nitrogen economy by providing a practical, efficient, cost-effective, and environmentally friendly solution for treating NO_3^- rich wastewater. Future research should focus on optimizing the ECSN system's performance and extending its applicability to treat various wastewaters, thereby offering a more energy-efficient and sustainable solution for industrial wastewater treatment and ammonia recovery.

Competing interests

The authors declare no competing interests.

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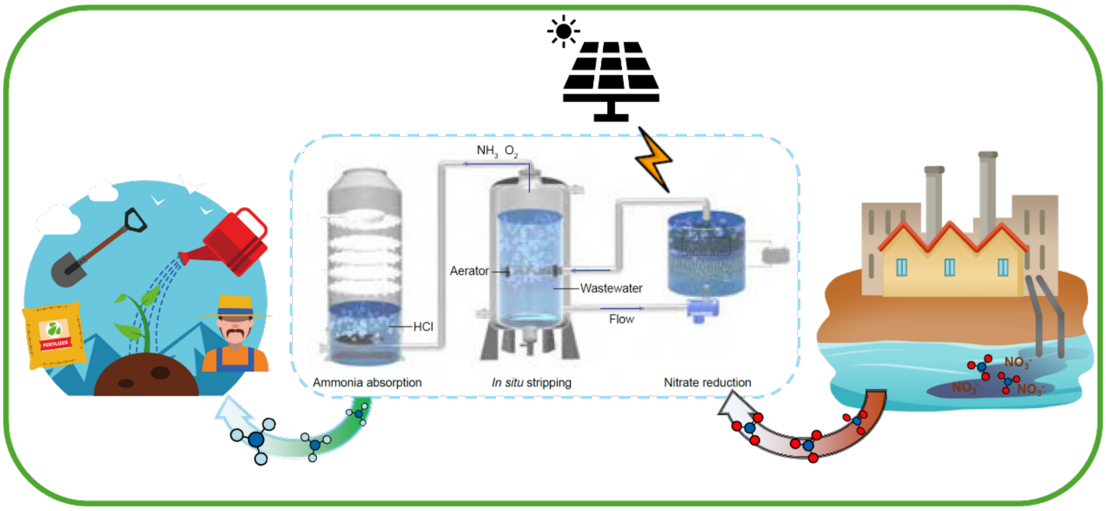

Fig 1. Schematic diagram of electrochemical reduction of nitrate in wastewater to economically valuable ammonia using renewable energy.