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# Combining Electrochemical Nitrate Reduction and Anammox for Treatment of Nitrate-Rich Wastewater: A Short Review

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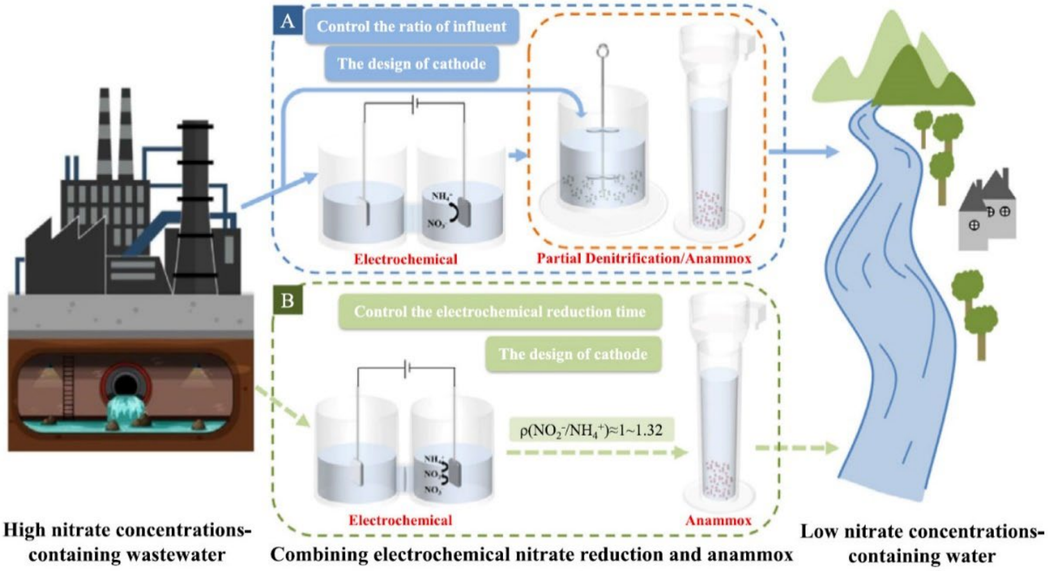
## Abstract

Treatment of nitrate-rich wastewater is important but challenging for the conventional biological denitrification process. Here, we propose combining the electrochemical reduction and anaerobic ammonium oxidation (anammox) processes together for treatment of nitrate-rich wastewater. This article reviews the mechanism and current research status of electrochemical reduction of nitrate to ammonium as well as the mechanism and applicability of the anammox process. This article discusses the principles, superiorities, and challenges of this combined process. The feasibility of the combined process depends on the efficiency of electrochemical nitrate reduction to ammonium and the conditions in the anammox process to use the reduced ammonium as the substrate to achieve

deep nitrogen removal. The article provides a feasible strategy for using the electrochemical reduction and anammox combined process to treat nitrate-rich wastewater.

## Graphical Abstract



**Keywords:** nitrate-rich wastewater, electrochemical nitrate reduction, anammox process, nitrogen removal

## 1. Introduction

Nitrate-contaminated water/wastewater is mostly found in industrial wastewater, such as from electroplating, fertilizer, and explosives industries, which may lead to eutrophication of surface water, damage to aquatic ecosystems, and increases in health risks related to nitrate/nitrite (Ghafari et al., 2008; Mohajeri et al., 2021; Zhang et al., 2021). For example, gastrointestinal microorganisms can reduce nitrates to nitrites, leading to gastric cancer and methemoglobin (also known as Blue Baby Syndrome) (Forman et al., 1985; Powlson et al., 2008). Although biological nitrification/denitrification processes are most widely used as traditional nitrogen removal technology (Thakur and Medhi, 2019), they have several major shortcomings. Nitrification is energy intensive, while the follow-up denitrification often needs an external organic carbon source for complete nitrate reduction. Suitable ratios of carbon to nitrogen (C/N) of 2.7–3 are required to reduce nitrate (Chung et al., 2014). For wastewater of a low C/N ratio, the need for extra organic carbon addition would lead to a sharp increase in cost (Hu et al., 2020). In addition, some industries or communities only consider the discharge standard of ammonium in the past, instead of total nitrogen (TN), and thus only convert ammonium into nitrate in effluent, resulting in discharge of nitrate-rich (e.g., 50 to 500 mg N/L of nitrate) wastewater (Li et al., 2012). Nowadays, China's wastewater discharge standards have been improved: the Discharge Standard of

Water Pollutant for Nitric Acid Industry specifies the discharge of TN (Li et al., 2012). Therefore, it is imperative to develop an efficient and flexible process to realize deep nitrogen removal of nitrate-rich wastewater.

Nitrogen removal technology based on anammox has been a research hotspot because of the various advantages, such as no additional carbon source, low sludge production, low energy consumption, low cost, and higher nitrogen removal rate (NRR) (Adams et al., 2020a; Jin et al., 2012; Pereira et al., 2017). Autotrophic nitrogen removal technologies as a single process for nitrogen removal have been developed and have attracted much attention, such as partial short-cut nitrification and denitrification, partial nitrosation-anammox (PN-A), and complete autotrophic nitrogen removal, restriction of autotrophic nitrification and denitrification, demonification, simultaneous partial nitrification, anammox and denitrification and bio-augmentation batch enhanced, etc. (Kartal et al., 2011; Kartal et al., 2010; Nsenga Kumwimba et al., 2020; Sliekers et al., 2002; van Kempen et al., 2001). These processes usually need ammonium as a substrate to achieve efficient nitrogen removal without adding external organic carbon. For nitrate-rich wastewater, nitrate should be first converted to ammonium with another method in order to employ these techniques.

As a nitrate reduction method of high catalytic efficiency, the electrochemical nitrogen reduction method uses electrons provided by power supply (as green reducing agents) to selectively reduce nitrate to ammonium, nitrite, nitrogen, etc. Therefore, the differential electrochemical reduction of nitrate based on the target product mainly consists of nitrate reduction to nitrogen and/or ammonia (C. Li et al., 2020; Q. Wang et al., 2017). The most attractive advantages of the method are the efficient and flexible synthesis of the target product by selecting cathode material and optimizing operation parameters (Li et al., 2009; Tokazhanov et al., 2020).

Accordingly,we hypothesize that a process combining electrochemical reduction and anammox (thereby called an electrochemical-anammox process) would be perfect for treatment of nitrate-rich wastewater. Currently, there is no available information on how to combine the two processes and how to control process parameters to guarantee the reliability of the combined process for complete nitrogen removal. In the past few years, many scholars have developed a series of various bimetallic materials to selectively reduce nitrate to $N_2$, thus achieving nitrate removal. However, it is difficult to convert nitrate to $N_2$ as the N—N coupling reaction is quite difficult and competes with the facile kinetics to $NH_4^+$/$NH_3$ and $H_2$ (Canfield et al., 2010; Rosca et al., 2009). Moreover, it is doubtful that the use of expensive electrode catalysts can really support the high selectivity for $N_2$ (Chen et al., 2015). Zhou et al. (2021) proposed the electrocatalytic-chlorine (EC-Chlorine) system to realize two-stage conversion ($NO_3^- \rightarrow NH_4^+ \rightarrow N_2$). However, this electrocatalytic-active chlorine process requires the use of highly efficient anode materials for ammonium oxide.

The objective of this article is to provide a feasible strategy for the application of the electrochemical-anammox process for nitrogen removal. This article first reviews the mechanism and current research status of using an electrochemical reduction process to reduce nitrate to ammonium, then analyzes the anammox processes for nitrogen removal with a focus on identifying and controlling the critical factors (e.g., a suitable anammox substrate ratio of $NH_4^+$-N/$NO_2^-$-N) to achieve deep nitrogen removal with an annamox process, and finally discusses applicability and challenges of the combined process for treatment of nitrate-rich wastewater.

## 2. Electrochemical reduction of nitrate to ammonium

Figure 1 shows the principle of electrochemical reduction of nitrate to ammonium. In this reduction process, the reduction efficiency of nitrate is associatedwith the theoretical potential of thermodynamics,which is mainly limited or affected by nitrate concentration and electrode material on the kinetics.

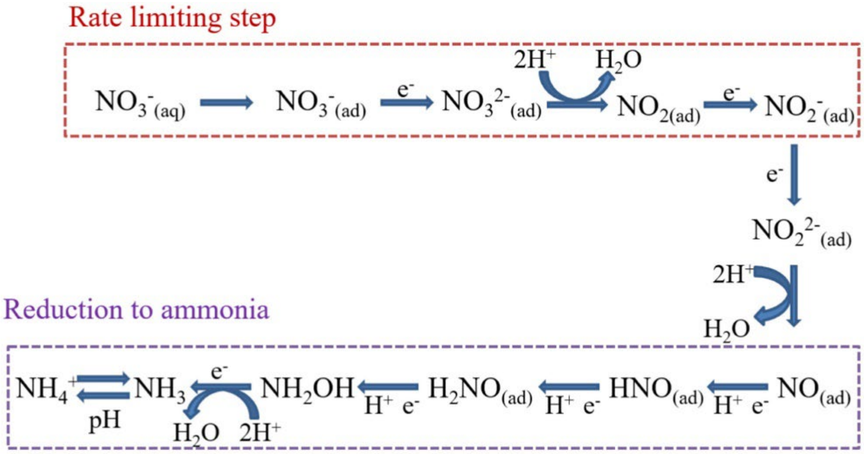


**Figure 1.** The mechanism of reduction of nitrate to ammonium (Zeng et al., 2020). Copyright 2020, Wiley.

### *2.1. Pathways and mechanisms*

The nitrogen is known to go through several different oxidation states spanning from +5 to −3 in reduction of nitrate-nitrogen to ammonium with various reaction intermediates and products being involved (e.g., ammonia, nitrite, hydrazine, hydroxylamine, nitric oxide, nitrous oxide) (Garcia-Segura et al., 2018; Zhang et al., 2021). The ammonia ($NH_3$) is one of the most thermodynamically stable forms of nitrogen under standard conditions and also is one of the indispensable substrates of the anammox process. The substance produced by Equation (1) is considered to be one of the preferred final products.

$$NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O \quad (1)$$

$E^0 = -0.12$ V versus Standard Hydrogen Electrode (SHE)

In addition, the reduction of nitrate to nitrite is considered as one of rate-limiting step,which plays a decisive role in the kinetics of the overall reaction (Eq. (2)).

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \qquad E^0 = 0{:}93\text{V versus SHE} \quad (2)$$

Although the electrochemical reduction of adsorbed (ad) nitrate to nitrite can be described with Equation (2), the generation of nitrite often includes a three-step electrochemical-chemical-electrochemical mechanism (Garcia-Segura et al., 2018). In detail, the initial electrochemical reduction generates a short-lived (≈20 μs) nitrate di-anion radical ($NO_3^{2-}$) according to Equation (3) (Cook et al., 2001). The first electron transfer reaction occurs at a significantly negative potential, and a Tafel slopes of 120 mV $dec^{-1}$ supports the premise that the first electron transfer is the rate-determining step (Dima et al., 2003). The slow kinetics are attributed to the high energy of the lowest unoccupiedmolecular π* orbital (LUMO π*) of nitrate, which makes charge injection into the π* orbital highly unfavorable (da Cunha et al., 1996). Then, the $NO_3^{2-}$ is hydrolyzed to nitrogen dioxide radical ($NO_2$•) by a homogenous chemical reaction (Eq. (4)). Consequently, $NO_2$• is further reduced to $NO_2^-$ adsorbed on the substrate via the second electron transfer reaction, as shown in Equation (5).

$$NO_{3(ad)}^{-} + e^{-} \rightarrow NO_{3(ad)}^{2-} \qquad E^0 = -0.89\ \text{V versus SHE} \tag{3}$$

$$NO_{3(ad)}^{2-} + 2H^{+} \rightarrow NO_2\bullet + H_2O \qquad k = 5.5 \times 10^4\ s^{-1} \tag{4}$$

$$NO_2\bullet_{(ad)} + e^{-} \rightarrow NO_{2(ad)}^{-} \qquad E^0 = 1.04\ \text{V versus SHE} \tag{5}$$

With the further reduction of nitrite, the adsorbed state of nitric oxide (NO) is formed and progressed to ammonium. First, nitrite is charged to form the ion radical $NO_2^{2-}$ according to Equation (6), and the $NO_2^{2-}$ is rapidly hydrolyzed via Equation (7) to NO due to the instability of $NO_2^{2-}$. Then, NO got an electron to produce HNO under acidic conditions via Equation (8). The produced HNO is further reduced to $H_2NO$ according to Equation (9), which also plays a dominant role in the pathway of subsequent reactions. After Equation (9), Equation (10) occurs due to rapid charge transfer, releasing hydroxylamine ($NH_2OH$), which is protonated to form $H_3NOH^+$ according to Equation (11). Finally, the $NH_3$ is produced by the rapid electrochemical reduction of $NH_2OH$ (Eq. (12)), but the balance between $NH_3$ and ammonium is determined by the pH of system (Eq. (13)) (Zeng et al., 2020).

$$NO_{2(ad)}^{-} + e^{-} \rightarrow NO_{2(ad)}^{2-} \qquad E^0 = -0.47\text{V versus SHE} \tag{6}$$

$$NO_{2(ad)}^{2-} + H_2O \rightarrow NO_{(ad)} + 2OH^{-} \qquad k = 1.0 \times 10^5\ s^{-1} \tag{7}$$

$$NO_{(ad)} + H^{+} + e^{-} \rightarrow HNO_{(ad)} \qquad E^0 = -0.78\text{V versus SHE} \tag{8}$$

$$HNO_{(ad)} + H^{+} + e^{-} \rightarrow H_2NO_{(ad)} \qquad E^0 = 0.52\text{V versus SHE} \tag{9}$$

$$H_2NO_{(ad)} + H^{+} + e^{-} \rightarrow H_2NOH_{(ad)} \qquad E^0 = 0.90\text{V versus SHE} \tag{10}$$

$$H_2NOH + H^{+} \rightarrow H_3NOH^{+} \qquad pKa = 5.93 \tag{11}$$

$$H_2NOH + 2H^+ + 2e^- \rightarrow NH_3 + H_2O \qquad E^0 = 0.42\text{ V versus SHE} \tag{12}$$

$$NH_3 + H^+ \rightarrow NH_4^+ \qquad pKa = 9.25 \tag{13}$$

In summary, the mechanisms for electrochemical reduction of nitrate to ammonium are highly complex, involving many intermediates, and stable intermediates (e.g., $NO_2$, $NO_2^-$, NO, $N_2O$, $N_2$, $NH_2OH$, and $NH_3$) can be generated. For example, in alkaline solution, products are $NO_2$, NO, and $NH_2OH$, whereas in acidic solution, products are $N_2O$, $NH_4^+$, $N_2$, etc. However, $N_2$ and $NH_3$ are the main forms due to their high thermodynamic stability, and their ultimate selectivity is mainly determined by the electrode materials (Rosca et al., 2009; Zhang et al., 2021).

The electrochemical reduction process involves nitrate adsorption, electron transfer, product desorption, and separation based on the kinetic mechanisms (Zeng et al., 2020). The kinetic rate is mainly controlled by the rate at which the reactants are adsorbed on the electrode surface. Therefore, the conformation of nitrate adsorbate depends on the electrode materials, nitrate concentration, etc. For example, with different nitrate loading, the electrode kinetic order varies. Dima et al. (2003) compared the CV curves of Pt and Rh electrode at different nitrate concentrations (0.001, 0.005, 0.01, 0.05, and 0.1 M); they reported that the reduction current increased with the nitrate concentration (Rh is more significant than Pt), and the mode of butterfly-like hydrogen adsorption and desorption finally disappeared under acidic conditions when the concentration of nitrate was 0.1 M, revealing the active surface area was occupied by nitrate adsorbents. In order to catalyze nitrate reduction with slow kinetics based on the economical choice of the catalyst, the type of electrode catalyst is gradually changed from noble metal electrodes to non-noble metal electrodes, such as nanosheet $Bi_2O_3$/carbon cloth (Chen et al., 2021), nanosheet $Co_3O_4$/Ti (C. Li et al., 2020), etc. In addition, the crystal plane of the electrode could not be neglected.

### *2.2. Factors influencing performance and selectivity of electrochemical reduction of nitrate to ammonium*

#### *2.2.1. Nitrate concentration*

According to the reduction mechanism of nitrate, the initial process of nitrate reduction is the adsorption of nitrate on the electrode surface, and the adsorption efficiency is closely related to the nitrate concentration. Under a low nitrate loading rate (e.g., 50 mg/L nitrate), a 98.8% conversion of nitrate to ammonium can be achieved with a Pd—Cu $(OH)_2$/CF cathode with an excellent nitrate-N reduction rate (0.017 $cm^2$/min). With an increase in nitrate loading, higher ammonia transformation can be achieved by reasonable selection of catalyst (Zhou et al., 2021). Chen et al. (2020) used 500 mg/L nitrate as a substrate for electrolysis with copper-incorporated crystalline 3,4,9,10-perylenetracarboxylic dianhydride as the catalyst for the reduction of nitrate to $NH_3$, and the $NH_3$ generation efficiency and maximum Faradaic efficiency could reach 97.8% and 85.9% at −0.4 V versus reversible hydrogen electrode (RHE). An electrochemical process allowing the efficient conversion of nitrate (3000 mg/L) solutions to ammonium in neutral media has been reported, and the maximum ammonium selectivity could reach to 96% at a current efficiency of 72% with a flow rate of 2 mL/min and an $i_{app}/i_{th}$ ratio of 1 (Abdallah et al., 2014).

In summary, the Faraday efficiency of ammonia can bemaintained at a high level due to the extensive electrochemical processes regardless of nitrate loading. Of course, nitrate concentration also directly affects the order and type of chemical kinetics and the activation point on the electrode surface. Based on Langmuir's kinetic equation (Eq. (14)), Katsounaros and Kyriacou (2008) established the kinetic equation of nitrate reduction (Eq. (15)):

$$\mathrm{M}^+ + \mathrm{NO}_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M}\cdots\mathrm{NO}_3 \xrightarrow{k} \mathrm{Products} \tag{14}$$

$$-\frac{\mathrm{d}[\mathrm{NO}_3^-]}{\mathrm{dt}} = k[\mathrm{M}^+] + \frac{K[\mathrm{NO}_3^-]}{1+K[\mathrm{NO}_3^-]} \tag{15}$$

where $K$ ( $= k_1/k_{-1}$) is the ion association constant,which indicates that nitrate tends to form ion pairs. Equation (15) indicates that the reduction follows zero-order kinetics when the concentration of nitrate is high, because $1 + K[NO_3^-] \approx K[NO_3^-]$ and first-order kinetics when the concentration of nitrate is sufficiently low as $1 + K[NO_3^-] \approx 1$. Katsounaros and Kyriacou (2008) also demonstrated that the reduction reaction follows zero-order kinetics within the first 75 min at a nitrate concentration of 62,000 mg/L (1 M) and can be sufficiently described by first order kinetics at 6200 mg/L (0.1 M). This phenomenon may be due to the blockage of the electrode surface sites, resulting in a reduction rate of nitrate (Ureta-Zañartu and Yáñez, 1997). In addition, when the concentration of nitrate is more than 62,000 mg/L (1M), the ability of nitrate to compete for surface position was better than other anions, so the reaction rate was hardly affected. In order to alleviate the influence of nitrate concentration on the reduction process, the selection of catalyst and the preparation of electrode materials could not be ignored.

### *2.2.2. Cathode material*

The cathode is most important for the selective reduction of nitrate to ammonium by electrochemical methods, especially for its electrocatalytic activity and selectivity (Table 1). The electrocatalytic activity of gold (Au) electrodes modified with thiourea (TU), urea (U), iodide ion ($I^-$), and sulfide ion ($S^{2-}$) has been used. The results showed that TU/Au had the highest current efficiency (about 85%) compared with U/Au, $I^-$/Au, or $S^{2-}$/Au electrodes in 31,000 mg/L (0.5 M) nitrate with pH of 12.5. The TU molecules adsorbed on the surface of Au electrode (which have a neutral charge at pH of 12.5) would not hinder the enrichment of nitrate ions on the electrode surface to form $NH_3$ with the highest catalytic efficiency; this is because the hydrogen evolution reaction (HER) of different cathodes was restricted by TU, resulting in the enrichment of $H_{(ads)}$ on the surface of Au with an increased selectivity for $NH_3$ (El-Deab, 2004). The more economical titanium (Ti) electrode is able to achieve high selectivity for $NH_3$ at high concentrations of protons and nitrate (Fig. 2A), which achieves high Faradaic efficiency (82.0%) of $NH_3$ in the presence of 24,800 mg/L (0.4 M) nitrate (McEnaney et al., 2020). Deng et al. (2021) constructed a Co-NAs electrode for electrochemical nitrate reduction in order to overcome the difficulty of practical application due to the low current density (Fig. 2C), which showed the higher current density of −2.2 A/cm$^2$ and $NH_3$ production rate of 10.4 mmol/h/cm$^2$. This unprecedented nitrate reduction efficiency benefits from the tight attachment of highly active substances within the $Co^0$ to the conductive substrate material and the exposure of a large number of active sites in the nanostructure.

**Table 1.** The electrocatalytic reduction of nitrate to ammonia or ammonium

| Cathodes | $NO_3^-$ concentrations | Electrolytes | Parameters | Conversion efficiency | References |
|---|---|---|---|---|---|
| TU/Au | 31,000 mg/L $NO_3^-$ | 0.25 mol/L $Na_2SO_4$ | pH: 12.5<br>$N_2$-saturated<br>Reduction peak: +0.75 V versus RHE | Ammonia production: about 85% | (El-Deab, 2004) |
| Ti | 24,800 mg/L $NO_3^-$ | — | Potential: −1 V versus RHE | Faradaic efficiency toward ammonia: 82% | (McEnaney et al., 2020) |
| Rich oxygen vacancies ($TiO_{2-x}$) | 50 mg N/L $NO_3^-$ | 0.5 mol/L $Na_2SO_4$ | Applied potential: −1.6 V versus SCE | Faradaic efficiency toward Ammonium: 85.0% Ammonium selectivity: 87.1% | (Jia et al., 2020) |
| $Bi_2O_3$ nanosheet/ carbon cloth | 50 mg/L $NO_3^-$ | 0.5 mol/L $Na_2SO_4$<br>0.1 mol/L $H_2SO_4$ | pH: 3.5<br>Current density: 10 mA/cm$^2$ | Ammonia selectivity: 80.3%<br>Nitrate reduction reaction efficiency:84.9% | (Chen et al., 2021) |
| Pd-$Cu(OH)_2$ | 50 mg/L $NO_3^-$ | 0.1 mol/L PBS | pH: 7<br>Potential: −1.2 V versus SCE | Ammonium generation efficiency: 98.8%<br>Nitrate removal rate: 0.017 cm$^2$/min | (Zhou et al., 2021) |
| Cu/$Cu_2O$ NWAs | 200 mg N/L $NO_3^-$ | 0.5 mol/L $Na_2SO_4$ | Optimal potential: −0.85 V versus RHE | Nitrate conversion rate: 97.0%<br>Ammonia yield rate: 0.2449 mmol/h/cm$^2$<br>Faradaic efficiency toward ammonia: 95.8%<br>Ammonia selectivity: 81.2% | (Y. Wang et al., 2020) |

**Table 1.** *Continued*

| Cathodes | $NO_3^-$ concentrations | Electrolytes | Parameters | Conversion efficiency | References |
|---|---|---|---|---|---|
| Cu@$Cu_{2+1}$O NWs | 50 mg N/L $NO_3^-$ | 0.5 mol/L $K_2SO_4$ | Potential: −1.2 V versus SCE<br>Electrolytic time: 2 h | Ammonia-N selectivity: 76% | (Ren et al., 2021) |
| Cu (111) nanosheets | 620 mg/L $NO_3^-$ | 0.1 mol/L KOH | Overpotential: −0.15 V versus RHE | Ammonia formation rate: 390.1 μg/mg Cu/h Faradaic efficiency toward ammonia: 99.7% | (Fu et al., 2020) |
| Copper-incorporated crystalline 3,4,9,10-perylenetracarboxylic dianhydride | 500 mg/L $NO_3^-$ | 0.1 mol/L phosphate buffer solution (PBS) | pH: 7<br>Optimal potential: −0.4 V versus RHE | Ammonia production rate: 436 ± 85 μg/h/cm²<br>Ammonia generation efficiency: 97.8%<br>Faradaic efficiency toward ammonia: 85.9% | (Chen et al., 2020) |
| Graphite felt/Cu | 3000 mg/L $NO_3^-$ | 0.25 mol/L PBS | pH: 7.2<br>Flow rate: 2 mL/min<br>Applied current ($i_{app}$)/calculated intensity ($i_{th}$): 1 | Ammonium selectivity: 96% | (Abdallah et al., 2014) |
| Cu/GO/Ti | 140 mg N/L $NO_3^-$ | 0.05 mol/L $Na_2SO_4$ | Current density: 15 mA/cm² | Ammonium selectivity: 63.6% | (J. Wang et al., 2020) |
| $Cu_3P$/CF | 50 mg N/L $NO_3^-$ | 0.05 mol/L $Na_2SO_4$ | Potential: −1.2 V versus SCE<br>Electrolytic time: 5 h<br>pH = 7 | Ammonium generation efficiency: ≈ 80% | (Yao et al., 2021) |
| Cu NSs/NF | 140 mg/L $NO_3^-$ | — | Potential: −1.1 V versus SCE | Ammonium generation efficiency: 99.7% | (T. Wu et al., 2019) |
| Co-Nas | 6200 mg/L $NO_3^-$ | 0.1 mol/L KOH | Potential: 0.11 to −0.24 V versus RHE | Faradaic efficiency toward ammonia: > 96% | (Deng et al., 2021) |

**Table 1.** *Continued*

| Cathodes | $NO_3^-$ concentrations | Electrolytes | Parameters | Conversion efficiency | References |
|---|---|---|---|---|---|
| $Co_3O_4$/Ti | 100 mg N/L $NO_3^-$ | 0.05 mol/L $Na_2SO_4$ | Electrolytic time: 1.5 h Current density: 10 mA/cm$^2$ | Ammonium generation efficiency: ≈ 70%<br>Nitrate removal efficiency: ≈ 100% | (Su et al., 2017) |
| CuO - $Co_3O_4$/Ti | 100 mg N/L $NO_3^-$ | 0.05 mol/L $Na_2SO_4$ | Electrolytic time: 1.5 h Current density: 20 mA/cm$^2$ | Ammonium generation efficiency: 65.8% | (C. Li et al., 2020) |
| $Co_3O_4$ -$TiO_2$/Ti | 50 mg/L $NO_3^-$ | 0.1 mol/L $Na_2SO_4$ | pH = 7 Electrolytic time: 100 min Current density: 25 mA/cm$^2$ | Ammonium generation efficiency: ≈ 90% | (Gao et al., 2019) |
| $Pt_{78}Ru_{22}$/C | 7440 mg/L $NO_3^-$ | 1 mol/L $H_2SO_4$ | Potential: −0.1 V versus RHE | Faradaic efficiency toward ammonia: > 93% | (Z. Wang et al., 2021) |
| Strained Ru nanoclusters | 62,000 mg/L $NO_3^-$ | 1 mol/L KOH | Potential: −0.2 V versus RHE | Ammonia-evolving selectivity: ≈ 100% | (J. Li et al., 2020) |
| Graphite felt | 124 mg/L $NO_3^-$ | 0.01 mol/L NaCl | Potential: −1.8 V versus SCE Electrolytic time: 2 h | Nitrate removal efficiency: 70%<br>Ammonium selectivity: 34% | (Ding et al., 2015) |
| BDD | 65 mg N/L $NO_3^-$ | 0.1 mol/L $Na_2SO_4$ | pH: 6.0 ± 0.2 Electrolytic time: 4 h Constant current density: 40 mA/cm$^2$ | Nitrate removal efficiency: 96.3%<br>Ammonium selectivity: 43.6% | (Ghazouani et al., 2015) |

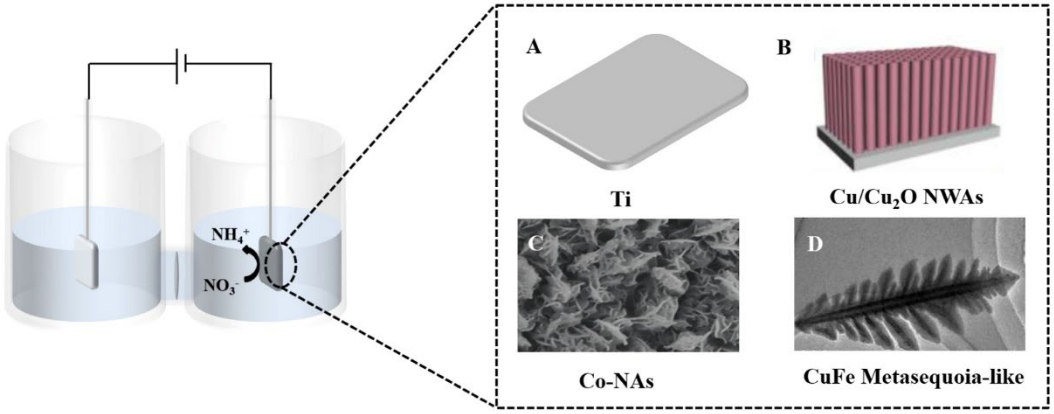


**Figure 2.** Representative cathode materials in the electrochemical reduction of nitrate to ammonia. (A) Titanium electrode (McEnaney et al., 2020), (B) Cu/$Cu_2O$ NWAs electrode (Y. Wang et al., 2020) Copyright 2020,Wiley, (C) Co-NAs electrode (Deng et al., 2021) Copyright 2021,Wiley, (D) CuFe Metasequoia-like electrode (C. Wang et al., 2021) Copyright 2021,Wiley.

During the past decades, extensive research has been conducted on using Cu electrodes for nitrogen reduction reaction due to high catalytic performance of Cu. However, the stability of Cu electrodes should be further confirmed in terms of the structures and electrochemical performance. In this context, synthesizing Cu nanocatalysts of different configurations has been found to be a feasible way to further improve catalytic performance. In addition, the CuO nanowire arrays (CuONWAs) were transformed to form Cu/$Cu_2O$ nanowire arrays, which had a higher electrochemically active surface area (ECSA) than CuONWAs (Fig. 2B), indicating excellent activity, selectivity, and Faradaic efficiency for electrocatalytic nitrate reduction to $NH_3$ (NRA). The electrode could achieve a 97.0% conversion efficiency of nitrate, a $NH_3$ yield of 0.2449 mmol/h/cm$^2$, Faradaic efficiency of 95.8% and $NH_3$ selectivity of 81.2% at the optimal potential (−0.85 V versus RHE), respectively (Y. Wang et al., 2020). In addition, compared to nanocubes, nanoparticles, and metal foils, the Cu (111) nanosheets had a higher current density in the rate control step of reducing nitrate to nitrite due to the rational design of the crystal face. The electrode material showed high activity ($NH_3$ formation rate: 390.1 μg/mg Cu/h) and high selectivity (Faradaic efficiency: 99.7%) at a low overpotential of −0.15 V versus RHE, which was because the Cu (111) nanosheets could inhibit the activity of HER and accelerated the rate of determination step (Fu et al., 2020).

Alloy electrode materials and nonmetallic materials will be the basis of industrial application in the future because of the high cost of metal electrode and its poor corrosion resistance in the process of nitrate reduction to ammonium. For example, it has been reported that graphite felt has a higher nitrate reduction efficiency (70%) and corrosion resistance than that of Cu—Ni and Ti, but its ammonia selectivity is only 34% in 2 h (Ding et al., 2015). The selectivity of nonmetallic materials to ammonium is not satisfactory. A metasequoia-like nanocrystalline $Cu_{49}Fe_1$ catalyst has been reported for electrochemical nitrate reduction to ammonia in neutral medium (Fig. 2D), exhibiting a faradaic efficiency up to 94.5% and a good $NH_3$ selectivity of 86.8% due to the Fe-shifted Cu d-band center for enhanced adsorbability of the intermediate (C. Wang et al., 2021). The applicability of this material was restricted by the stability and cost of electrocatalysis. A Cu/Ti alloy deposited on graphene oxide was selected as the cathode electrode to achieve a suitable accumulation efficiency of ammonium (63.6%), improving the economy and stability of alloy materials (J. Wang et al., 2020).

## 3. Anaerobic ammonium oxidation (anammox) process

### *3.1. The mechanism of anammox*

The anammox is one of autotrophic nitrogen removal processes, oxidizing ammonium under hypoxic conditions, with nitric oxide (NO) and hydrazine ($N_2H_4$) as intermediates, and nitrite as the electron acceptor to generate to nitrogen ($N_2$) (Fig. 3, Anammox—red line path).

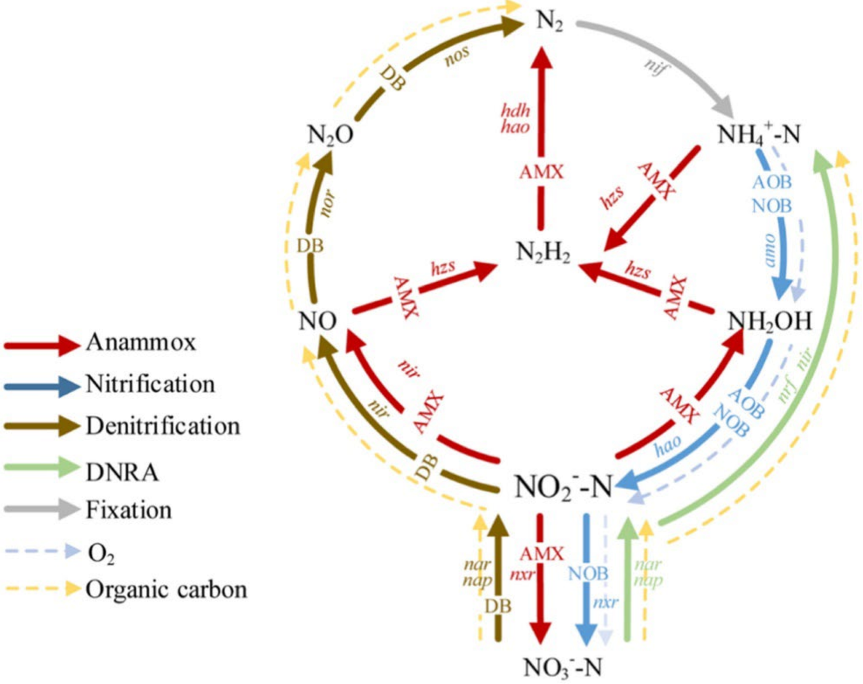


**Figure 3.** The mechanics of anammox (red line path) (Wu et al., 2020). Copyright 2020, IWA Publishing.

As shown in Equation (16) (Adams et al., 2020b), the reaction can realize the whole process of autotrophic nitrogen removal without organic carbon source. Compared with traditional nitrification/denitrification technology, the process can reduce aeration volume of 100%, organic carbon source of 100%, and operating cost of 90% (Adams et al., 2021; He et al., 2015; Li et al., 2018a), produce a lower sludge yield and reach higher nitrogen removal efficiency. The anammox process has been a research hotspot in the field of wastewater treatment (Ruiz et al., 2003).

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 0.066CH_2O_{0.5}N_{0.15} + 2.03H_2O \quad (16)$$

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \quad (17)$$

### *3.2. Partial denitrification (PD)*

Ammonium has been accumulated in the front-end electrochemical process, and nitrite is produced by partial denitrification process. At present, the partial denitrification (PD) has become a way for nitrite production. Under the action of denitrifying bacteria, incomplete denitrification can lead to the accumulation of nitrite-N. This process is called NIR partial denitrification. As shown in Equations (18) and (19), the final reduction product of nitrate-N is fixed in nitrite-N (Du et al., 2019).

$$NO_3^- + 0.083C_6H_{12}O_6 \rightarrow NO_2^- + 0.5CO_2 + 0.5H_2O \quad (18)$$

$$1.32NO_3^- + 0.55CH_3COO^- + 0.088NH_4^+ + NO_2^- \rightarrow 1.32NO_2^- + 0.088C_5H_7NO_2 + 0.66HCO_3^- + 0.198H^+ + 0.264H_2O \quad (19)$$

Some researchers developed the rapid initiation of PD through pH control in a pilot-scale test. The results showed that within 100 cycles, the PD process could be established rapidly at pH of 9.0. After stabilization, the average nitrate to nitrite conversion rate (NTR) was 83.86% (Si et al., 2018). The formation of PD granular sludge could further increase the NTR. Studies found that PD always maintained a high nitrite production (average NTR of 88.3%) during the granulation process in the sequencing batch reactor (SBR) with nitrate of 60 mg N/L (Cao et al., 2019). In addition, the activity of key enzymes (nitrate reductase (NAR) and nitrite reductase (NIR)) could also be used to evaluate the performance of PD. At 20 mg/L $NH_2OH$, the enzymatic reaction rate of the key enzyme (NAR) increased by 1.17 times compared to processeswithout $NH_2OH$, and the activity of NIR increased by 75.26 ± 1.15% at this concentration (Zhang et al., 2020). At the laboratory scale, the anammox in the combined process could be achieved by the accumulation of nitrite via PD. Considering the economics, there is no doubt that the formation of granular sludge is more desirable than the addition of $NH_2OH$ to provide an appropriate amount of nitrite accumulation in the practical water treatment process.

### *3.3. Critical factors*

The anammox bacteria (AnAOB) required specific conditions to achieve optimal performance. The crucial influence factors include pH, temperature, dissolved oxygen, and organic concentration, etc. (Li et al., 2018b; Ma et al., 2016). However, since the high nitrate-rich wastewater is discharged mainly as the industrial wastewater, the critical factors that deserve most considerations are the ratio of substances and adaptability in the performance of the combined electrochemical reduction and anammox process.

### *3.3.1. The ratio of substrates*

Nitrite and ammonium are the two main substrates involved in an anammox process and have an important influence on the AnAOB activity. The synergistic removal efficiency of the nitrite and ammonium is also the most important indicator of the performance of anammox. In 1977, Broda (1977) first predicted that the anammox reaction could be catalyzed by lithotrophic bacteria. Based on thermodynamic calculations, taking into account of evolutionary changes and thermodynamic principles, Broda (1977) predicted that chemosynthetic bacteria could use oxygen or nitrate as oxidant to oxidize ammonium to $N_2$ (see Eq. (12)). Until 1998, Strous et al. (1998) proposed the widely accepted anammox stoichiometry. However, the optimal substrate ratio for anammox may depend on different reactors, operating conditions, and microorganisms. For example, Strous et al. (1999) suggested that 2.0 was the optimal ratio for $NO_2^-$-N/$NH_4^+$-N in key physiological studies at anammox. Jin et al. (2013) found the optimal ratio to be 1.2 in the anammox process of the up-flow biological filter. However, the optimum ratio was considered to be 1.0 in the filter media-on-anammox composite reactor for the treatment of nitrogenous wastewater. In summary, the nitrogen removal performance of anammox is directly affected by the change of matrix ratio; the ratio of $NO_2^-$-N/$NH_4^+$-N, which is theoretically involved in anammox, might be 1–1.32.

### *3.3.2. Adaptability*

The anammox technology is considered to be one of the most promising nitrogen removal methods since the discovery of anammox bacteria. The world's first industrial-scale anammox reactor was built in Rotterdam, the Netherlands, in 2002 (van der Star et al., 2007) and pioneered the application of anammox technology in the field of wastewater nitrogen removal. At present, the anammox technology has been successfully applied to the treatment of nitrogen-containing wastewater, especially in the treatment of industrial wastewater with obviously high ammonium concentration and insufficient carbon sources (Anfruns et al., 2013). Among them, sludge-digestion liquid, landfill leachate and urban domestic sewage are typical representatives of the applicable anammox technology.

The sludge-digestion liquid had been facing challenges because of the high ammonium concentration (500–2000 mg N/L) and a large amount of refractory organic matter (2000–3000 mg/L). The removal efficiency of ammonium (influent was 2100–2200 mg N/L) could reach up to 98% when combining with partial nitrification, complete ammonia oxidation (comammox) and anammox processes. These results were considered to be the synergistic nitrogen removal of ammonium oxidizing bacteria (AOB), nitrite oxidizing bacteria (NOB), *Candidatus Kuenenia*, and *Nitrospira* in the process, and the *Candidatus Kuenenia* was the dominant AnAOB with a relative abundance of 0.10% (L. Wu et al., 2019).

It is difficult to treat landfill leachate that contains relatively high concentrations of ammonium (usually >1000 mg N/L), dissolved organic matter (DOM) (mainly including volatile fatty acids (VFAs) and aquatic humic substance (AHS)) and salinity, etc. (Liang et al., 2009). The total removal efficiency of ammonium (influent was 168 ± 2 mg N/L) could reach 94% with the partial nitritation-anammox (PN/A) process in landfill leachate treatment;

ammonia oxidizers, heterotrophic denitrifiers, and anammox bacteria were all contributed to the conversion of nitrogen in landfill leachate. The 16S rRNA amplicon sequencing revealed that the *Planctomycetes* (10–31%)was the dominant phyla, and the most abundant genus was *Candidatus Brocadia* (7–25%), a well-acclaimed genus among AnAOB (Podder et al., 2020).

In addition, the anammox technology has also been applied to the urban domestic sewage treatment. The partial nitrification (PN)-simultaneous anammox and denitrification (SAD) process was used to remove nitrogen in urban domestic sewage. The result showed that the nitrogen removal efficiency of municipal sewage (COD = 164.2 ± 33.1 mg/L, ammonium = 52.1 ± 3.6 mg N/L, nitrite = 0.1 ± 0.2 mg N/L, nitrate= 1.1 ± 0.6 mg N/L) could reach 97.1%; the total inorganic nitrogen (ammonium, nitrite, and nitrate) in the effluent was only 1.6 ± 0.8mg N/L; anammox process was accounted for as much as 73–82% in nitrogen removal process, of which *Candidatus Brocadia* (accounting for 8.0–2.2%) was the dominant bacteria at genus (Deng et al., 2020). The anammox technology has also been applied to treat other wastewaters besides the three types of wastewater, such as coke-oven wastewater, monosodium glutamate wastewater, pharmaceutical wastewater, etc. (Jin et al., 2012) (Table 2).

**Table 2.** Various types of wastewater treatment efficiency based on Anammox process

| Types of wastewater | Process | Influent | Removal | References |
|---|---|---|---|---|
| Sludge-digestion liquid | Partial-nitrification<br>Complete ammonia oxidation (comammox)<br>Anammox | Ammonium: 2100–2200 mg N/L | Ammonium removal efficiency: 98.82% | (L. Wu et al., 2019) |
| Sludge-digestion liquid | Denitrification (DN)<br>Partial nitrification (PN)<br>Anammox | Ammonium: 300–400 mg N/L | Total nitrogen: < 20 mg N/L<br>NRR: 0.85 kg N/$m^3$/day | (X. Li et al., 2020b) |
| Sludge-digestion liquid | Partial nitrification Anammox (PN/A) | Ammonium: 1060–1200 mg N/L | NRR: 1.23 kg N/$m^3$/day | (G. Wang et al., 2017) |
| Sludge-digestion liquid | Partial nitritation Anammox | Ammonium: 1400–1600 mg N/L<br>Total nitrogen: 1600–2200 mg N/L<br>Nitrogen loading rate: 5.3 kg N/$m^3$/day | NRR: > 4.0 kg N/$m^3$/day | (Furukawa et al., 2009) |
| Sludge-digestion liquid | Partial nitritation Anammox | Nitrogen loading rate: 10 kg N/$m^3$/day | NRR: 9.5 kg N/$m^3$/day | (Jin et al., 2013) |

**Table 2.** *Continued*

| Types of wastewater | Process | Influent | Removal | References |
|---|---|---|---|---|
| Landfill leachate | Partial nitritation Anammox (PN/A) | COD: 950 ± 10 mg/L<br>Ammonium: 168 ± 2 mg N/L | Ammonium removal efficiency: 94%<br>COD removal efficiency: 26% | (Podder et al., 2020) |
| Landfill leachate | Step-feed<br>Partial nitrification<br>Simultaneous anammox Denitrification (SPNAD) | Ammonium: 1000 ± 250 mg N/L<br>Soluble chemical oxygen demand (SCOD): 1100 ± 200 mg/L<br>Total nitrogen: 1300 ± 75 mg/L | Nitrogen removal efficiency: 98.7%<br>NRR: 0.23 kg N/m$^3$/day | (F. Zhang et al., 2019) |
| Landfill leachate | Partial nitrification-anammox<br>Partial-denitrification-anammox (NADA) | COD: 1400–2000 mg/L<br>Ammonium: 460–500 mg N/L | Total nitrogen removal efficiency: > 95%<br>Ammonium removal efficiency: > 95% | (Wu et al., 2018) |
| Landfill leachate | Denitrification (DN)<br>Partial nitrification (PN)<br>Anammox | Ammonium: 2550 ± 200 mg N/L<br>COD: 2500 ± 250 mg/L | Total nitrogen removal efficiency: 96.7%<br>NRR: 0.46 kg N/m$^3$/day | (X. Li et al., 2020a) |
| Urban domestic sewage | One-stage anammox | COD: 100 mg/L<br>Ammonium: 60 mg N/L<br>Total nitrogen: 70 mg/L | COD removal efficiency: 89%<br>Ammonium removal efficiency: 96.7%<br>Total nitrogen removal efficiency: 70% | (Wei et al., 2020) |
| Urban domestic sewage | Partial nitrification (PN)<br>Simultaneous anammox and denitrification (SAD) | COD: 164.2 ± 33.1 mg/L<br>Ammonium: 52.1 ± 3.6 mg N/L | Total inorganic nitrogen: 1.6 ± 0.8 mg N/L<br>Nitrogen removal efficiency: 97.1% | (Deng et al., 2020) |
| Urban domestic sewage | Enhanced biological phosphorus removal (EBPR)<br>Partial nitritation-anammox (PN/A) | COD: 160–320 mg/L<br>Total nitrogen: 42–67 mg/L<br>Soluble chemical oxygen demand (SCOD): 120–180 mg/L<br>Ammonium: 36–58 mg N/L<br>Total phosphorus: 3.0–8.7 mg/L | Total phosphorus: 0.25 mg/L<br>Total nitrogen: 10.8 mg/L | (Yang et al., 2017) |

**Table 2.** *Continued*

| Types of wastewater | Process | Influent | Removal | References |
|---|---|---|---|---|
| Pharmaceutical wastewater | Sequential biocatalyst addition (SBA)<br>Anammox | Ammonium: 123–257 mg N/L<br>Nitrite: 133–264 mg N/L<br>COD: 415–843 mg/L | Ammonium: < 50 mg N/L<br>NRR: 9.4 kg N/m$^3$/day | (Tang et al., 2011) |
| Monosodium glutamate wastewater | Partial nitrification<br>Anammox (PN/A) | COD: 2000–2500 mg/L<br>Ammonium: 1500–2000 mg N/L<br>$SO_4^{2-}$: 5000–5500 mg/L | Nitrite removal efficiency: > 70%<br>Ammonium removal efficiency: > 69% | (Shen et al., 2012) |
| Synthetic coking wastewater | Single-stage simultaneous carbon oxidation<br>Partial nitritation<br>Denitritation<br>Anammox | Ammonium: 400 mg N/L<br>COD: 800 mg/L<br>Phenol: 200 mg/L | Phenol removal efficiency: 99.8%<br>Total nitrogen removal efficiency: 89.8% | (Zhou et al., 2020) |
| Petrochemical wastewater | Anammox | COD: 235–703 mg/L<br>Ammonium: 90–210 mg N/L<br>SS: 40–250 mg/L | Ammonium removal efficiency: 85%<br>Nitrite removal efficiency: 90% | (An et al., 2013) |

## 4. The proposed combined process: principles, superiorities, and challenges

### *4.1. Principles of combined process*

As a method of high catalytic efficiency, the electrochemical nitrate reduction not only can use electron as green reducing agent to selectively reduce nitrate to ammonium but also has high flexibility in the treatment of different concentrations of nitrate. In addition, anammox could remove ammonium-nitrogenwith no addition of external carbon, low sludge production, low energy consumption, low cost, and higher NRR. Therefore, we hypothesize that, in an electrochemical-anammox process, the anammox process could use the reduction product of electrochemical nitrogen reduction as a substrate to achieve deep nitrogen removal with autotrophic process.

Figure 4A shows the proposed electrochemical-anammox process, where a part of the high nitrate-rich influent is shunted to the front-end electrochemical process. The high selectivity of ammonium will be achieved by rational selection of cathode catalyst. Then, the two wastewaters mix together in the PD system. The operating parameters of the PD will be optimized to achieve the accumulation efficiency of ammonium and nitrite and to meet the subsequent anammox substrate ratio for achieving deep nitrogen removal. The key to this combined process is the regulation of the influent shunt ratio and the reasonable design of electrode material.

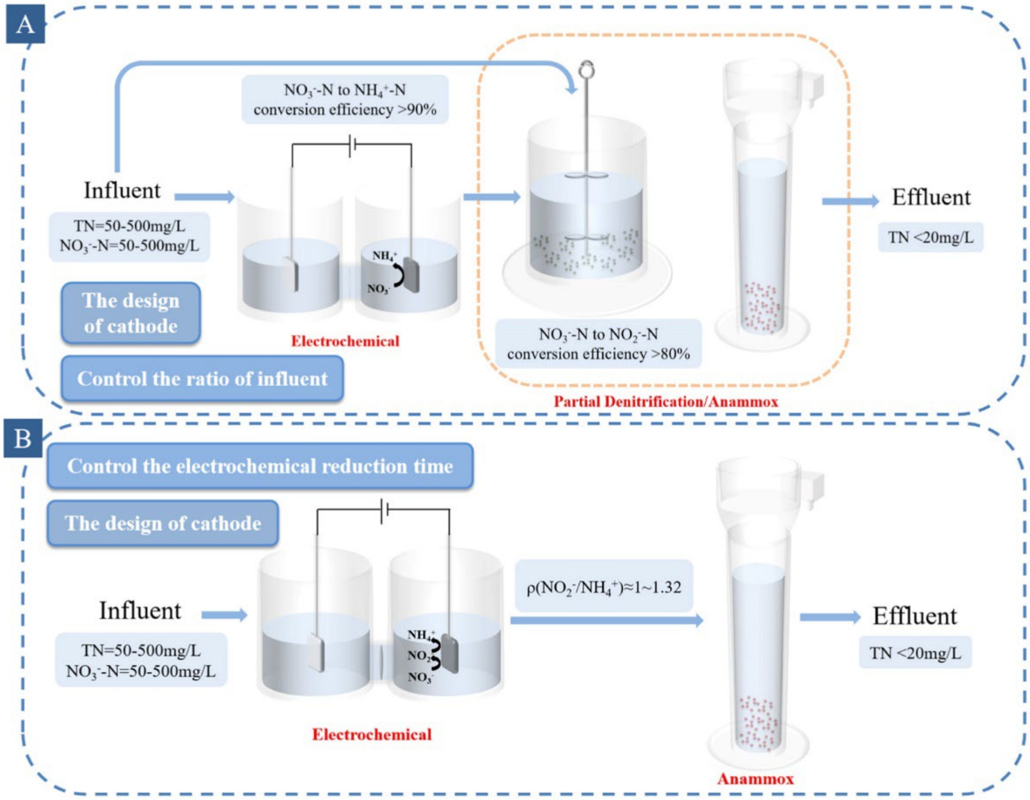


**Figure 4.** Electrochemical-anammox process technical vision. (A) Electrochemical-partial denitrification/anammox, (B) electrochemical-anammox.

In a recent study, an oxide-derived silver (OD-Ag) cathode has a unique and ultra-high selectivity in the conversion of nitrate to nitrite. The results showed that the selectivity of nitrite is up to 98% under a wide potential window (Liu et al., 2021). Highly selective nitrites (95%) were also reported in another study using Cu (100) as a cathode for nitrate reduction (Roy et al., 2016). Consequently, a combined process–simultaneous electrochemical reduction of nitrates to achieve high selectivity for ammonium and nitrite to meet the optimum substrate ratio of anammox was emerged based on the above highly ammonium selective electrode. However, the construction of dual electrochemistry leads to a sharp increase in complexity and cost. Further reduction of ammonium with nitrite may improve the process (discussed below).

Figure 4B shows the above-mentioned electrochemical-anammox process, where 100% of the high nitrate-rich influent is introduced into the front-end electrochemical process. In view of the excellent selectivity of nitrates to nitrites in the above electrodes, the accumulated nitrite can be further reduced to ammonium. A suitable anammox ratio ($\varrho(\mathrm{N0}_2^-\text{-N})/\varrho(\mathrm{NH}_4^+\text{-N}) \approx 1$–1.32) can be achieved by controlling the electrochemical reduction time and designing a reasonable catalyst. Then, it is combined directly with the anammox to achieve deep nitrogen removal. The key of this combined process is the reasonable design of electrode material and the control of reduction time.

### *4.2. Superiorities of combined process*

The novel combined electrochemical-anammox technology offers a promising alternative to mitigating the shortcomings of the traditional denitrification process. The following features of the combined electrochemical-anammox technology are pivotal:

- The electrochemical reduction of nitrate technology has stronger resistance to a shock loading, which could reduce nitrate efficiently and rapidly due to the high specific surface area and numerous catalytic sites of the electrode materials.
- The electrochemical reduction of nitrate technology has high flexibility and universality, which could greatly reduce the amount of carbon input and does not need precise control of temperature and C/N ratio compared with the denitrification process.
- The anammox technology has the characteristics of low carbon, emission reduction, and consumption reduction, which could reduce organic carbon source by 100%, sludge yield by 90%, and greenhouse gases emissions by 90%.
- The anammox technology is more adaptable to the type of wastewater, such as coke-oven wastewater, monosodium glutamate wastewater, and pharmaceutical wastewater.

### *4.3. Challenges of combined process*

Although significant progress has been made in catalyst construction, product control, and mechanism research, the following challenge still limits the practical application of combining electrochemical nitrate reduction and anammox, such as impurity ions, pH, large-scale electrode, inhibitors, economy, etc.

#### *4.3.1. Impurity ions*

The nitrate reduction rate was influenced by the presence of anion ($SO_4^{2-}$, Cl–, etc.) and cation ($Li_+$, $Na_+$, $K_+$, etc.) electrolytes, the impurity ions could enhance the electrical conductivity in the wastewater, reducing the operation cost. On the one hand, the impurity anions also compete with nitrate for adsorption sites at the surface electrodes or affect the magnitude of electrostatic hindering effect (the characteristic enthalpy of adsorption of each anion on a specific metal cathode) (Dima et al., 2003). In particular, 5% to 20% saline containing NaCl will activate the process of electro-chlorination, demonstrating the high selectivity of $N_2$ evolution. Zhou et al. (2021) proposed an electro-catalytic chlorine (EC-chlorine) system to support this theory. As mentioned above, the formation of active chlorine requires highly efficient and expensive electrode materials compared to the anammox process. On the other hand, impurity cations provide balanced positive charge centers that attract nitrates to form neutral ions, inhibiting electrostatic repulsion between the cathode and nitrates (both negatively charged) (Katsounaros and Kyriacou, 2008). Furthermore, the formed electrolyte can be used as redox medium to propagate an indirect electrochemical reaction, which could increase the rate of nitrate reduction.

### *4.3.2. pH*

In this combined process, both the electrochemical reduction of nitrate and anammox process are affected by pH. pH can also influence the selectivity and kinetics of the electrochemical reduction of nitrate, but the effect may vary based on the electrode material and the electrolyte. C. Li et al. (2020) used a $Co_3O_4$/Ti cathode with a nanosheet structure to remove nitrate and found that the generation of $NH_3$-N increased obviously when pH was adjusted to 7. In comparison, the reduction efficiency of nitrate with zero-valent titanium at pH = 4 was optimal (Yao et al., 2019). Meanwhile, the optimum pH range for AnAOB is 6.7–8.3 due to its high sensitivity to pH (Tang et al., 2009). Therefore, in the selection of electrode materials, it is also necessary to pay attention to whether the pH of the solution adapts to the growth and activity of AnAOB when the generation efficiency of ammonium is appropriate.

### *4.3.3. Large-scale electrode*

Since the most research has concentrated on the laboratory-scale highly efficient reduction of nitrate electrode materials, sufficient information still is not available on the preparation method, expansion, and stability of the electrode material for field-scale applications of the combined process. The non-noble metal alloy material is known as an efficient promoter for nitrate electro-reduction based on the aforementioned studies. The synthesis methods mainly include sol-gel (C. Li et al., 2020), electrodeposition (J. Wang et al., 2020), and hydrothermal (Ma et al., 2018). Electrodeposition is mainly used to deposit particle metal on the substrate, which has the advantages of low cost and fabrication of large area (Musiani, 2000). However, the practical application of that method is limited by the reduction of active sites due to particle aggregation and heterogeneous deposition (Ning et al., 2019). The sol-gel method can be used at normal temperature, and the chemical composition of the product can be precisely controlled. However, the method is relatively time-consuming, and involves the use of some organic solvents harmful to humans (Rane et al., 2018). As a simple method, the hydrothermal method also has the limitation of reliability and reproducibility (Tavakoli et al., 2007).

On the other hand, the stability and service life of carbon-based materials such as graphene oxide modified electrode materials have been significantly improved (J. Wang et al., 2020). The stability of Ti and Ti-GO electrodes was tested by chronoamperometry measurements, and the results show that the current density of a Ti-GO electrode is 2.13 times higher than that of a Ti electrode after 1000s running (Ma et al., 2018). Moreover, after 8 cycles of a CuNi/multi-walled carbon nanotube/graphite felt (CuNi−1.3/M/GF) cathode in a dual-chamber cell, Cu and Ni are hardly dissolved, and the nitrate removal efficiency remains above 80% (Lu et al., 2021). Therefore, the stability and difficulty of preparation of the large-scale electrode could not be ignored.

### *4.3.4. Inhibitors*

The anammox process is inhibited by many factors, such as organics, heavy metals, antibiotics, salinity, etc. (Jin et al., 2012). It has been widely reported that a small amount of the inhibitors can enhance the tolerability and activity of AnAOB (Lu et al., 2019; X. Zhang et al., 2019a; X. Zhang et al., 2019b). In contrast, AnAOB activity was significantly limited by the high-concentration of the inhibitor, and construction of anammox granular sludge may be a feasible strategy (Izadi et al., 2021). Extracellular polymeric substance (EPS) from anammox granular sludge interacts with the cells through complex interactions to form a network that acts as the first barrier to prevent inhibitor from penetrating the cells (Sheng et al., 2013; Zhang et al., 2018). The long-term effects of antibiotics on the specific anammox activity (SAA) using amoxicillin, florfenicol, and sulfamethazine were analyzed. The results of the study indicated that the SAA levels decreased by approximately half within the first 3 days, but the SAA levels gradually recovered to pre-antibiotic stress with an increase in EPS production of anammox granular sludge (Zhang et al., 2015).

### *4.3.5. Economic analysis*

Based on the above factors and challenges, the electrode material is always the key to the electrochemical reduction of nitrate to ammonium. Therefore, the cost of electrode materials and energy consumption are critical to the application of this process. For example, assuming nitrate concentrations are reduced from 100 to 20 mg N/L by denitrification, and each kg of nitrate-N removed from the waste stream costs 3.1 kg of methanol (at \$0.33/kg) and generates 0.372 kg of additional solids to be disposed at \$331/dry metric ton (Vineyard et al., 2020), the denitrification process is approximately \$9.88/m$^3$ (not including unknown pumping requirements). For the electrochemical reduction of nitrate process, total operating cost was calculated on the basis of total electrode cost and total electrical energy cost. Energy consumption has been mentioned in many studies. Yang et al. (2020) using a CuO-$Co_3O_4$/Ti cathode to treat nitrate observed the energy consumption cost of \$0.04/g TN. Moreover, the energy consumption of the Cu/Ti electrode (0.82 kWh/g nitrate-N, higher than Cu/GO/Ti electrode, 0.47 kWh/g nitrate-N) by electrochemical reduction of nitrate (J. Wang et al., 2020). However, few researchers have reported electrode cost analysis of practical wastewater; the cost of using Ti/$RuO_2$ (anode), Fe (cathode) as electrode can be calculated as \$286.25/m$^3$ for 49.24% of TN removal efficiency (Chauhan and Srivastava, 2020). In summary, the economics of the electrochemical reduction of nitrates is not satisfactory, but its high efficiency and flexibility as well as the combination of high efficiency and economic anammox process are enough to cover the difficulties in the selection and preparation of electrode materials. Therefore, great efforts are required to evaluate the cost of non-noble metal materials or non-metallic materials in the future research on the treatment of nitrate-rich wastewater by electrochemical reduction.

## **5. Summary**

With the increasing attention to environmental problems and the improvement of wastewater discharge standards, the high concentration of nitrate was difficult to remove by traditional biological nitrogen removal process. The electrochemical method could reduce nitrate to ammonium directional controlled manner without carbon source addition and sludge generation. The high selectivity of ammonium is based on the thermodynamic reduction potential, and it is hoped to construct a kind of non-noble metal materials such as nanosheet $Bi_2O_3$/carbon cloth with multi-active sites, high stability, and high specific surface area, facilitating a concerted proton and electron transfer. Compared with nitrate electro-catalytic reduction of nitrogen, the main advantage of process is that it can use low-cost non-precious metal materials and is less constrained by the mass balance on nitrogen atoms. At the same time, the combination process of electrochemical reduction and anammox does not require the use of anode materials with highly efficient ammonium oxide as compared with the combined process of electrocatalytic-active chlorine, and the deep nitrogen removal can be achieved by economical and green biological method. Therefore, the novel combined electrochemical-anammox technology has the advantages of strong impact load resistance, high flexibility, extensiveness, low carbon, emission reduction, and consumption reduction.

By taking a forward outlook, combining electrochemical nitrate reduction and anammox is promising in treating nitrate-rich wastewater. The process can be further boosted under the optimization and characterization of electrode materials. Although challenges remain in the application and parameter control of practical wastewater, we believe that the development of process has practical significance from the perspectives of environmental protection.

**Declaration of competing interest** – We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work; there is no professional or other personal interest of any nature or kind in any product, service, and/or company that could be construed as influencing the position presented in, or the review of, this manuscript.

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