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Electrochemical nitrate reduction to produce ammonia integrated into wastewater treatment: Investigations and challenges

Xinyi Zou[a], Jiawei Xie[a], Changhong Wang[b], Guangming Jiang[c], Kai Tang[a], Chongjun Chen[a,d,e,*]

[a] *School of Environmental Science and Engineering, Suzhou University of Science and Technology, Suzhou 215009, China*
[b] *School of Materials Science and Engineering, Suzhou University of Science and Technology, Suzhou 215011, China*
[c] *Engineering Research Center for Waste Oil Recovery Technology and Equipment, Ministry of Education, Chongqing Technology and Business University, Chongqing 400067, China*
[d] *Jiangsu Collaborative Innovation Center of Technology and Material of Water Treatment, Suzhou 215009, China*
[e] *Tianping College of Suzhou University of Science and Technology, Suzhou 215009, China*

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ABSTRACT

Nitrate (NO_3^-) is widely found in wastewater, which is harmful to human health and water environmental. Electrochemical reduction can convert NO_3^- to high value-added ammonia (NH_3)/ammonium (NH_4^+) for pollutant removal and resource recovery. Currently, electrochemical nitrate reduction to produce ammonia (ENRA) is mostly focused on the preparation of high-performance catalysts, while ignoring the prerequisite for industrial application as the stable operation and optimal regulation of the process. Therefore, the review focused on wastewater treatment, based on the mechanism of electrochemical nitrate reduction for ammonia production and reactor construction (reactor, power supply system), then summarized the operation control strategies (such as reduction potential, nitrate concentration, inorganic ions, pH) that should be noted for ENRA. Finally, the challenges (system structure, economy) and prospects (ammonia recovery process, construction of large-scale ENRA system, application of real wastewater) of the field as it moves towards commercialization were discussed. It is hoped that this review will facilitate the scaling up of ENRA in the wastewater treatment field.

1. Introduction

Nitrate (NO_3^-) is one of the most widespread water pollutants in the world, which may lead to eutrophication of surface waters, disruption of aquatic ecosystems and increasing risk of nitrate/nitrite-related diseases [1]. The methods currently used were biological and physical chemistry (*e.g.*, electrodialysis, reverse osmosis, ion exchange resins, and hydrogen catalytic reduction) method to remove nitrate form wastewater [2]. In addition, the most widely used method is still the traditional biological nitrification/denitrification technology. However, the traditional biological process not only requires sufficient organic carbon sources, but also generates CO_2 [3], and which was unable to meet the requirements with the advent of carbon neutralization and carbon peak. The energy conservation, emission reduction and resource recycling are the means to implement the concept of carbon neutrality [4].

As one of the most basic chemical raw materials, the ammonia (NH_3) plays an important role in agriculture, medicine, textile and other industries, and is also considered to have great potential as an important energy storage medium and carbon-free energy carrier [5]. At present, the industrial synthesis of NH_3 still relies on the century-old Haber-Bosch process. However, due to particularly harsh operating conditions (high temperature (400–500 °C) and high pressure (150–300 atm)), it has disadvantages such as high energy consumption, high cost, and high CO_2 emissions [6,7]. With the huge consumption of global energy, the people are committed to seek advanced renewable energy harvesting technologies, including solar energy, wind energy, geothermal energy, biofuels, *etc.* [8,9].

The electrochemical reduction of nitrate has attracted much attention due to its controllable reaction rate/selectivity, no need for chemical additives, and low-cost effectiveness [10]. The reduction of nitrate to ammonia is simpler than its reduction to nitrogen, which is attributed to the large overpotential (940.95 kJ/mol) re-

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* Corresponding author at: School of Environmental Science and Engineering, Suzhou University of Science and Technology, Suzhou 215009, China.
E-mail address: chongjunchen@163.com (C. Chen).

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quired to activate the N≡N bond energy of the N_2 molecule [11]. Meanwhile, ammonia as an attractive nitrogen source can be prepared as ammonia fertilizer to achieve a lower cost-benefit ratio (electricity cost/production value ≈ 0.5) [12,13]. On the other hand, electrochemical nitrate reduction to produce ammonia (ENRA) does not involve the use of H_2, which facilitates dispersive ammonium production at room temperature. And it can be combined with electricity from sustainable energy production [14]. Therefore, the ENRA technique that not only provides a measure for ammonia synthesis, but also eliminates nitrate pollution. On the other hand, the unavoidable problems of the large-scale application of ENRA are the design of the electrodes, the applicability of the real wastewater and the construction of the device [15,16] . Firstly, if the design of large-scale electrodes is proportionally enlarged, leading to problems such as increased internal resistance and uneven mass transfer [8,17]. The current mainstream solution is to design electrodes as stacked electrode modules [16]. Secondly, compared with synthetic wastewater, real wastewater contains a variety of substances (ions, organics, *etc.*), which will reduce the ammonia production efficiency of ENRA. Therefore, it is necessary to evaluate the influence (nitrate concentration, pH, impurity ions, *etc.*) on the ENRA system to provide a basis for the application of ENRA to real wastewater. Finally, traditional ENRA systems were generally dual-chamber batch flow reactors, which may lead to cumbersome system operations and surge in manufacturing costs if replicated in large-scale applications.

A number of previous related articles have focused on the research of electrode materials (*e.g.*, Cu, Co, Ag) [18–20]. For example, the high efficiency of metal catalysts for nitrate reduction were summarized [21], and non-noble metal electrocatalysts for nitrate reduction were reviewed [22]. However, for wastewater treatment, complex modified electrode materials led to a plummeting economic and industrial potential of the system. In order to promote ENRA system for scale up applications, the modification of electrode materials should be weakened and the focus should be on reactor operation and control strategies. Therefore, the review firstly expounded the reduction mechanism of ENRA, and then reviewed the reactor construction and regulation strategies (such as reduction potential, nitrate concentration, inorganic ions and pH). In addition, based on the difficulties faced by the practical application of ENRA process, the existed problems and challenges were summarized for better promotion and application.

2. Reaction mechanism of ENRA

Nitrogen has a broad valence state from +3 to −5, it exists stably in the form of nitrate-N (NO_3^-–N), ammonium-N (NH_4^+–N) and N_2 in nature [23]. The ENRA includes indirect and direct reactions, which are strongly related to the substrate concentration and the electrolyte acidity [24,25]. The indirect autocatalytic reaction only exists under the condition of nitrate concentration higher than 1 mol/L and low pH value, the nitrate not participate in the electron transfer in the reduction process (Eq. 1) [25]. However, most of the nitrate reduction reactions are mechanistically studied at concentrations below 1 mol/L (direct reaction), *via* both electron transfer reduction and atomic hydrogen reduction (Fig. 1) [22]. $NO_2^{\bullet}$ or NO^+ is the electroactive species involved in the direct reaction [26]. Nitrate (NO_3^-) undergoes a series of electron transfer processes, and the final product exists in the form of thermodynamically stable N_2 and ammonia (NH_3) [27]. The overall reaction equations are as follows Eqs. 2 and 3.

$$HNO_3 + 2H^+ + 2e^- \rightarrow HNO_2 + H_2O$$

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O, \tag{1}$$

$$E^o = 1.17\ \text{V}\ \textit{vs.}\ \text{standard hydrogen electrode (SHE)} \tag{2}$$

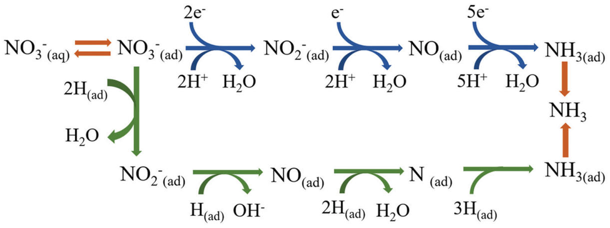

Fig. 1. The direct mechanism for electrochemical nitrate reduction mediated by electron transfer (blue arrow) and atomic hydrogen (green arrow).

$$NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O,\quad E^o = -0.12\ \text{V}\ \textit{vs.}\ \text{SHE} \tag{3}$$

Firstly, NO_3^- in the aqueous solution (aq) completes the initial adsorption on the electrode surface to form the NO_3^- in the adsorbed state (ad) (Eq. 4). Then, it is reduced to $NO_{2(ad)}^-$ through electron transfer (Eq. 5), which is considered a speed limit step. Because $NO_{3(ad)}^-$ has the high energy of the lowest unoccupied molecular π^* orbital (LUMO π^*), which makes charge injection into the π^* orbit very disadvantageous [1].

$$NO_{3(aq)}^- \rightleftharpoons NO_{3(ad)}^{2-} \tag{4}$$

$$NO_{3(ad)}^- + 2H^+ + 2e^- \rightarrow NO_{2(ad)}^- + H_2O \tag{5}$$

$NO_{2(ad)}^-$ can react rapidly on the electrode surface to produce $NO_{(ad)}$ (Eq. 6). A part of $NO_{(ad)}$ can be reduced to NH_4^+ (Eq. 7), and the other $NO_{(ad)}$ can also be desorbed from the electrode surface to generate $NO_{(aq)}$ (Eq. 8). The part of $NO_{(aq)}$ will form a weakly adsorbing NO dimer, and then further react to generate N_2O (Eq. 9), which is finally converted to N_2 (Eq. 10) [22].

$$NO_{2(ad)}^- + 2H^+ + e^- \rightarrow NO_{(ad)} + H_2O \tag{6}$$

$$NO_{(ad)} + 6H^+ + 5e^- \rightarrow NH_4^+ + H_2O \tag{7}$$

$$NO_{(ad)} \rightarrow NO_{(aq)} \tag{8}$$

$$NO_{(ad)} + NO_{(aq)} + 2H^+ + 2e^- \rightarrow N_2O_{(ad)} + H_2O \tag{9}$$

$$N_2O_{(ad)} + 2H^+ + 2e^- \rightarrow N_2 + H_2O \tag{10}$$

In addition, atomic hydrogen ($H_{(ad)}$) mediated reduction of nitrate can also occur under neutral or alkaline conditions [28]. First, water can be reduced by a Volmer process (Eq. 11) to produce $H_{(ad)}$ [29]. Then, $H_{(ad)}$ can be used as a strong reductant ($E^o(H^+/H) = -2.31$ V *vs.* SHE) to reduce intermediates ($NO_{3(ad)}^-$, $NO_{2(ad)}$ and $NO_{(ad)}$) and obtain $N_{(ad)}$ (Eqs. 12-14). Finally, $N_{(ad)}$ is reduced to $NH_{3(ad)}$ *via* Eqs. 15-17. The main reason for the final production in the form of NH_3 is that the N–H bond mediated by $H_{(ad)}$ is easier to obtain than the N–N bond [3].

$$H_2O + e^- \rightarrow H_{(ad)} + OH^- \tag{11}$$

$$NO_{3(ad)}^- + 2H_{(ad)} \rightarrow NO_{2(ad)}^- + H_2O \tag{12}$$

$$NO_{2(ad)}^- + H_{(ad)} \rightarrow NO_{(ad)} + OH^- \tag{13}$$

$$NO_{(ad)} + 2H_{(ad)} \rightarrow N_{(ad)} + H_2O \tag{14}$$

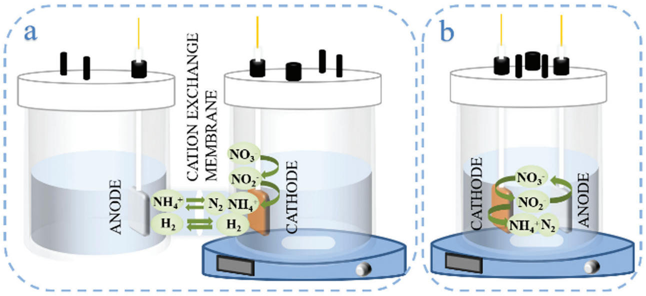

Fig. 2. (a) Single-chamber and (b) dual-chamber used in ENRA.

$$N_{(ad)} + H_{(ad)} \rightarrow NH_{(ad)} \tag{15}$$

$$NH_{(ad)} + H_{(ad)} \rightarrow NH_{2(ad)} \tag{16}$$

$$NH_{2(ad)} + H_{(ad)} \rightarrow NH_{3(ad)} \tag{17}$$

3. Reaction system construction

3.1. Reactor

3.1.1. Single-chamber cell

In a single reaction chamber (Fig. 2a), reactions that occur in pairs may favor nitrate removal. For example, NH_4NO_3 formed in single-chamber reactors can be recovered as fertilizer by reducing concentrated nitrate brines in agricultural runoff and industrial wastewater to NH_4^+. The initial cost estimate of the strategy is lower than the typical cost range of NH_4NO_3 [30]. On the other hand, the oxidant (HClO) produced on the anode surface can also be used for water purification. In addition, the single-chamber reactor often has lower internal resistance than dual-chamber reactor due to the absence of ion exchange membranes, and the small electrode spacing, simple and inexpensive to design. Respectively, reduction and oxidation reactions occur simultaneously at the cathode and anode surfaces [31]. Therefore, some reoxidation of the reduced intermediates on the anode surface usually occurs in the single-chamber reactor, reducing the Faradaic efficiency of ammonia. At the same time, the dissolved metal ions produced by the anode are also deposited on the cathode surface, changing the performance of the original cathode material for ENRA [32].

3.1.2. Dual-chamber cell

The dual-chamber electrochemical reactor (Fig. 2b) is composed of two chambers separated by ion exchange membranes or salt bridges, and is more versatile in design and mode of operation. A cation exchange membrane (*e.g.*, Nafion membrane) can electrostatically reject anions leading to the anode chamber. Therefore, the occurrence of side reactions can be overwhelmingly reduced to improve the Faradaic efficiency of ammonia. In addition, due to the physical separation between the two chambers, mixing of solutions between the chambers can be prevented at the same time. Thus, two different types of wastewaters can be treated in separate anode and cathode chambers for joint treatment, avoiding energy waste (The anodic cell can achieve the removal of refractory organics or the mineralization by anodic oxidation, and the electrons generated are used for the reduction of nitrate in the cathodic cell with the support of an external power supply system). As mentioned earlier, a dual-chamber reactor has a higher ohmic resistance than a single chamber, which can increase energy consumption. In general, the key is how to achieve the maximum balance between efficiency and economy.

3.2. Power supply system

3.2.1. Potentiostatic electrolysis

Potentiostatic electrolysis is achieved by applying a constant potential externally, which allows better control of the selectivity of nitrate reduction [33]. Therefore, in addition to the required working electrode and counter electrode, an additional reference electrode is usually required to control the electrode potential in addition to the working electrode and counter electrode. For example, in an electrochemical nitrate reduction reaction, the working electrode represents the cathode, where the reduction reaction occurs. The counter electrode acts as the anode. A complete circuit is formed between the cathode and the anode. The reference electrode is only used as a reference to measure and control the constant potential required for the cathode, as a half-cell with a known reduction potential. The commonly used reference electrodes are Ag/AgCl with saturated KCl ($E^o = +0.197$ V *vs.* SHE) electrodes or saturated calomel electrodes (SCE) $Cl^-/Hg_2Cl_{2(s)}/Hg_{(l)}/Pt$ ($E^o = +0.241$ V *vs.* SHE), but still using SHE ($E^o = 0$ V for $\alpha_{H^+} = 1$) as the reference standard [27]. In previous studies of nitrate reduction, it was found that the reaction usually takes place under overpotential conditions, which is a potential beyond that required by thermodynamic theory, and the overpotential needs to have a high activation energy [34]. High activation energy often leads to slower nitrate reduction compared with constant current electrolysis. Most importantly, the power supply conditions are more complicated in the three-electrode system, which makes it difficult to be applied in the field of wastewater treatment on a large scale.

3.2.2. Galvanostatic electrolysis

Galvanostatic electrolysis is achieved by applying a constant current. The current is expressed in the form of current density, which determines the electrodynamics of the reaction. Theoretically, a higher current density means that more electrons are available for nitrate reduction at the electrode interface, accelerating the conversion of nitrate. In addition, greater current density promotes the generation of H^*, which applies its indirect reduction pathway to increase the nitrate conversion efficiency. However, excessive cathodic currents can also intensify side reactions and generate more H_2. And the large number of bubbles affects the reaction between nitrate and electrode interface in water and reduces the electron utilization efficiency. As a result, the nitrate conversion rate cannot be significantly increased by continuing to increase the current [35,36]. Compared with the constant potential system, the constant current system does not require the participation of a reference electrode for control. It makes the system more promising for industrial applications. Of course, the lack of control over the reaction potential can lead to exacerbated side reactions that reduce the Faradaic efficiency of ammonia. Therefore, the anode potential needs to be determined before a constant current (applied voltage is supplied) to evaluate the constant applied voltage required. The ultimate purpose is that the determined constant current can maximize economic benefits and suppress the occurrence of side reactions.

4. Operation control strategy

There is no denying that electrode materials are of paramount importance in the production of ammonia from nitrate, and much has been written on the subject. However, the potential of expensive and complex electrode materials to be used in practical treatment is minimal in the field of wastewater treatment. Therefore, it is also important not to neglect the stable operation of the system and the operational control strategy (Fig. 3).

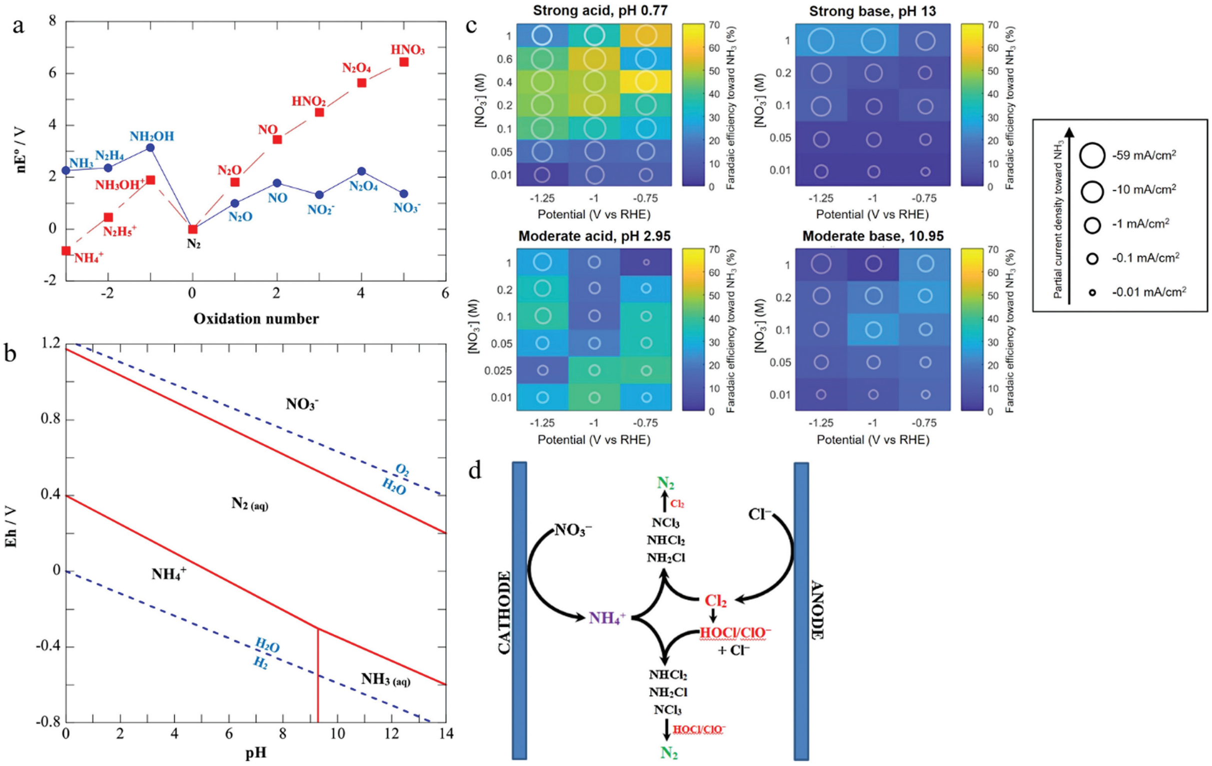

Fig. 3. (a) Frost-Ebsworth diagram of nitrogen species at pH 0.0 and pH 14.0. Copied with permission [27]. Copyright 2018, Elsevier. (b) Pourbaix diagram of nitrogen species. Copied with permission [27]. Copyright 2018, Elsevier. (c) Four distinct pH values showing Faradaic efficiency to NH_3 by varying applied potentials and nitrate concentrations. Copied with permission [30]. Copyright 2020, ACS Publications. (d) Influence Mechanism of electrochemical nitrate reduction to ammonia in presence of Cl^-. Copied with permission [27]. Copyright 2018, Elsevier.

4.1. Reduction potential

The electric potential is the main driver of electrochemical nitrate reduction and significantly affects the rate and products of nitrate reduction [37]. In kinetic perspective, electrochemical reduction of nitrate involves reactant diffusion, adsorption, charge transfer, product desorption and separation [21]. Polatides and Kyriacou [38] studied the kinetics of nitrate reduction reaction under $Sn_{85}Cu_{15}$ cathode and found that the increase in potential favored the formation of N_2 and NH_3. The rate of ammonia production increased more strongly when the potential was below −1.8 V (*vs.* Ag/AgCl). It is thought to require hydrogenation of the adsorbed NO for ammonia formation at high potentials, thus facilitating the rate of ammonia production with the increase in surface coverage of adsorbed hydrogen. Similarly, the CuO@PANI/NF cathode achieved the highest NO_3^-–N conversion efficiency (97.16%) at −1.3 V (*vs.* SCE). At this potential, the NH_3 yield, FE and selectivity all reached their peak (0.213 mmol h^{-1} cm^{-2}, 93.88% and 91.38%). Study at copper electrodes reduced the potential from −1.1 V to −1.2 V and then to −1.4 V (*vs.* Hg/HgO). The selectivity of ammonium first increased from 13% to 39% and then increased rapidly to 80% [39]. It was thought to be an inconsistent electron requirement for the different products, while Eqs. 2 and 3 also suggest that more negative potentials favor the production of ammonia. However, when the potential is too low, nitrate reduction is inhibited. When the potential decreased from −1.8 V to −2.0 V (*vs.* SCE), the nitrate reduction rate decreased from 15% to 8% after 120 min of electrolysis on the graphite cathode [40]. It was considered to be the effect of side reactions (*e.g.*, Hydrogen evolution reaction (HER)). The In-S-G catalyst exhibited a maximum NH_3 yield of 375 mmol g_{cat}^{-1} h^{-1} at −0.7 V (*vs.* RHE). The NH_3 yield remained around 321 mmol g_{cat}^{-1} h^{-1} when the potential dropped to −1.0 V (*vs.* RHE). However, the FE decreased from the peak of 75% (−0.5 V *vs.* RHE) to 36%. It was also thought to be caused by the competing processes of the HER at high potentials. In summary, the potential for studying the electrochemical nitrate production of ammonia usually lies between −0.8 V to −1.8 V (*vs.* SCE). The occurrence of side reactions can be suppressed to the maximum extent within the range, thus improving the selectivity of ammonia. Therefore, the optimal ammonia generation potential exhibited by different cathodes varies depending on the adsorption location and potential region of the material.

4.2. Nitrate concentration

In the field of wastewater treatment, there is a wide variety of nitrate-rich wastewaters and a wide range of nitrate concentrations. The nitrate concentration in municipal wastewater is mostly 10–200 mg/L NO_3^-–N, which is the prevailing range in the current research on electrochemical nitrate to ammonia [41]. For example, Pd $Cu(OH)_2$/CF as a cathode could produce up to 98.8% ammonium selectivity at 50 mg/L NO_3^- [42]. In contrast, under a higher nitrate concentration (500 mg/L NO_3^-), the ammonia production rate and efficiency also could reach 436 ± 85 μg h^{-1} cm^{-2} and 97.8%, respectively, using copper-incorporated crystalline 3,4,9,10-perylenetetracarboxylic dianhydride as the cathode material [43]. Some cathode materials with commercial application potential (*e.g.*, graphite felt and BDD) also exhibited impressive nitrate removal (70% and > 90%) in this NO_3^-–N concentration range (65–500 mg/L) [40,44].

Of course, many industries also produce high concentrations of nitrate-rich wastewater, such as cellophane, explosives, fertilizer, pectin and metal finishing industries, where the nitrate concentration even exceeds 1000 mg/L NO_3^-–N [41]. Similarly, electrochemical nitrate production of ammonia can also be accomplished at this concentration. Co-NAs catalysts achieved ammonia Faradaic efficiency of over 96% with the NO_3^-–N concentration of 2800 mg/L [6]. 14000 mg/L NO_3^-–N achieved 93%-98% faradaic efficiencies towards NH_3 production by ENRA with Pt_xRu_y [45].

Nitrate concentrations often directly affect the kinetic sequence of electrochemical reduction and the activation point of the catalyst surface. It is a conjecture based on the kinetic equations of nitrate reduction by Langmuir (Eq. 18), Katsounaros and Kyriacou (Eq. 19) [46].

$$M^+ + NO_3^- \underset{k_{-1}}{\overset{k_1}{\leftrightharpoons}} M \cdots NO_3 \xrightarrow{k} \text{Products} \tag{18}$$

$$-\frac{d\left[NO_3^-\right]}{dt} = k\left[M^+\right] + \frac{K\left[NO_3^-\right]}{1 + K\left[NO_3^-\right]} \tag{19}$$

where K ($= k_1/k_{-1}$) is the ionic association constant, indicating that nitrate tends to form ion pairs. The calculation of Eq. 19 shows that $1 + K[NO_3^-] \approx K[NO_3^-]$ in a high nitrate concentration environment and the reduction reaction follows zero-order kinetics. However, $1 + K[NO_3^-] \approx 1$ when the nitrate concentration is low enough, the first-order kinetics becomes the rule to be followed. To prove the conclusion, 62,000 mg/L (1 mol/L) and 6200 mg/L (0.1 mol/L) NO_3^- were used as conditions, respectively, with the former following zero-order kinetics within the first 75 min of the reaction, while the latter exhibited first-order kinetics [46]. The phenomenon may be attributed to the influence of intermediates and other ions, resulting in competition for the catalytic position on the electrode surface, where nitrate no longer dominates and thus the reduction rate decreases [47]. Therefore, nitrate is far more competitive than other ions when the concentration is greater than 62,000 mg/L (1 mol/L) NO_3^-, the reaction rate is almost unaffected. For example, the Strained Ru nanoclusters material was used to reduce 62,000 mg/L NO_3^- wastewater with ammonia selectivity close to 100% [48]. However, this type of wastewater is not particularly common, only nitric acid cleaning wastewater from nuclear weapons production plants and research laboratories for radioactive metal products, which can contain more than 50,000 mg/L NO_3^-–N [41]. Thus, high concentration has more potential when treating nitrate-rich wastewater for electrochemical ammonia production.

4.3. Inorganic ions

Significantly, the concentration and type of electrolyte affect the reduction of nitrate [49]. A portion of industrial and municipal wastewater has lower conductivity, even as low as 1 mS/cm [50]. Low conductivity tends to cause high charge transfer impedance of the system, which brings unnecessary economic losses. Therefore, the addition of salt and buffering agents (Na_2SO_4, NaCl, phosphate buffer saline) or application to high conductivity wastewater (landfill leachate) can effectively alleviate this defects [51].

In fact, the inorganic ions in wastewater are so complicated, such as SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, Na^+ and K^+. For example, cations can also act as "cation catalysts". The cation forms an instantaneous neutral ion pair by changing the bilayer structure of the cathode. And the ion pair can act as an attraction center for the reducing anion. The repulsion between anion and cathode is then weakened, thus aiding the reduction of nitrate at the cathode [52]. It was found that cations increase the rate of nitrate reduction along the trend of $Li^+ < Na^+ < K^+ < Cs^+$ [53]. Even higher rates than alkali metals can be obtained in the presence of multivalent cations such as NH_4^+, Ca^{2+} and La^{3+} [54]. On the other hand, the cation also has a certain influence on the product. Manzo-Robledo, Lévy-Clément and Alonso-Vante [55] found that the presence of K^+ makes N_2 the dominant product, while N_2O dominates in the presence of Na^+. HER was more difficult to occur in K^+-containing electrolyte solutions compared to Na^+, so the production of N_2 was less inhibited. The key factor is the adsorption of nitrogen in this study. It seems that the production of HER and nitrogen species is regulated by co-adsorption of alkali cations in the presence of alkali metal cations, while the variability of the products may be attributed to differences in the atomic radii of the Na^+ (99 pm), K^+ (138 pm). H^+ is continuously consumed at the cathode resulting in an increase in pH. Ca^{2+} and Mg^{2+} are adsorbed on the cathode surface and form precipitates, leading to poisoning of the active site of the cathode. In fact, their inhibition principles were different. Ca^{2+} and Mg^{2+} at a concentration of 1 mmol/L were distributed into the ENRA system, and it was found that calcium ions had a great influence on the selectivity of NH_4^+. The reason for this difference was that Ca^{2+} was mainly adsorbed to the catalyst surface to poison the active sites, but Mg^{2+} hindered ENRA by adhering to the cathode surface after being precipitated from the electrolyte [56].

Similarly, anions reduce the rate of nitrate reduction in the order $I^- > Br^- > Cl^- > F^-$ (@ −1.8 V) [53]. Because some anions compete for adsorption sites or influence the magnitude of the electrostatic hindrance effect (characteristic enthalpy of adsorption of each anion on a particular metal cathode), which affects the electrochemical reduction of nitrate [57]. I^- would not form ion pairs with cations, Cl^- could reduce the competitive reaction. But SO_4^{2-} would compete with NO_3^- for the active center on the electrode surface in a certain potential range [54,57]. Among them, Cl^-, which is present in large quantities in wastewater, also plays a distinctive role in electrochemical nitrate reduction. Easily, Cl^- reacts at the anode to produce HClO. It can be used not only for disinfection of water, but also for oxidation of NH_4^+ to produce N_2 [53,58].

4.4. pH

Nitrate-rich wastewater is widely distributed in ammunition industry/laboratories, pharmaceutical industry, mining sites, steel industry, electroplating and phosphorus industry, and the acidity and alkalinity of them vary [59]. For example, nitric acid which is commonly used in the electroplating industry to clean metals will produce a typically acidic wastewater, while wastewater from industries such as beverages, pulp, paper, and cement is mostly alkaline [60].

The electrochemical reduction of nitrate can occur over a wide pH ranging from highly acidic to highly basic, but its reduction kinetics and products vary at different pH [61–64]. Under acidic conditions, the HER reduces the Faradic efficiency of nitrate reduction because of competition for electrons [65,66]. Although the direct reaction of ENRA is affected by HER, the presence of indirect catalytic processes under acidic conditions can enhance the reduction kinetics [25]. However, the pH of the solution is not constant during the nitrate reduction process. The electrode interface and solution pH can even increase significantly as protons are consumed or hydroxides are produced [67–69]. During the process, the proton donor may change from H^+ to H_2O, when the base-catalyzed reaction is more favorable (the acid-catalyzed reaction is inhibited) [32]. In addition, pH has a profound effect in terms of product. Studies have shown that under alkaline conditions, nitrate reduction products are dominated by NO_2^-. The elevated proton concentration leads to the production of N_2, N_2O and NH_4^+ [70]. Similarly, Dortsiou, Katsounaros, Polatides and Kyriacou [71] observed that the main products were nitrogen, nitrous oxide and nitrite at pH > 4. Whereas, when pH between 0 and 4, ammonia and hydroxylamine were the main products. However, drastic changes in the pH of the solution pose the risk of altered reaction mechanisms. Ideally, highly concentrated buffer solutions can be used to mitigate changes in interface and solution pH.

Table 1
Application of electrochemical nitrate to ammonia in practical wastewater.

Types of wastewaters	NO_3^-–N concentration (mg/L)	Cathode material	Ammonia production	Nitrate removal efficiency	Potential/Current density/Current	Ref.
Chemical wastewater	241	$Ni(OH)_2$@Ni	Ammonia production efficiency: 92.5%	92.53%	Current density: 15 mA/cm^2	[16]
Chemical wastewater	506 ± 12	$Ni(OH)_2$@Ni	Ammonia production efficiency: 92.9%	94.66%	Current density: 20 mA/cm^2	[16]
Chemical wastewater	2527	$Ni(OH)_2$@Ni	Ammonia production efficiency: $>$ 92%	99.50%	Current density: 20 mA/cm^2	[16]
Concentrated surface water	1400	$Pd_{10}Cu$/BCN	Ammonia yield rate: 31154 μg h^{-1} mg_{cat}^{-1}	/	Potential: –0.6 V *vs.* RHE	[13]
Surface water	4.64	$Pd_{10}Cu$/BCN	/	≈95%	Current: 50 mA	[13]
Concentrated surface water	1400	BCN-Cu	Ammonia yield rate: 565.2 μg h^{-1} cm^{-2}	/	Potential: –0.3 V *vs.* RHE	[12]
Printing wastewater	208	CoP	Ammonia capture efficiency: 86% Ammonia recovery rate: 103 g NH_3–N m^{-2} day^{-1}	≈100%	Potential: 7 V	[75]
Concentrated surface water	1400	BCN@Ni	Ammonia yield rate: 801.0 μg h^{-1} cm^{-2}	/	Potential: –0.4 V *vs.* RHE	[76]
Outflowing wastewater from the water plant	3.47	Cu NRs	Ammonia production efficiency: 76.40%	97.69%	Potential: –0.6 V *vs.* RHE	[77]
Garbage fly ash washing wastewater after ion membrane treatment	17.04	Bi_2O_3/CC	Ammonia concentration: $>$ 20	≈86%	/	[78]
Explosive wastewater	22.6	Al	Ammonia production efficiency: 55.75%	44.64%	Current density: 166.67 A/m^2	[79]

4.5. Other factors

The stirring intensity of the reaction system also had a significant effect on the efficiency of nitrate reduction. The nitrate undergoes a reduction reaction on the cathode surface. The anion migrates towards the anode under the electric field, which is in the opposite direction to the mass transfer. Therefore, stirring can make the nitrate in the solution overcome the electric field repulsion and distribute it evenly, increasing the chance of contact between nitrate and cathode. At the same time, there is an equilibrium $NH_4^+ + H_2O \leftrightarrow NH_3 + H^+$ in the system [72], and vigorous stirring can help the reaction to occur continuously to the right. Reduction products from the cathode (*e.g.*, H_2) cover the surface of the electrode after a period of time. Stirring encourages these bubbles to escape, increasing the contact area between the nitrate and electrode. However, too vigorous stirring may affect the stability of the electrodes. From the perspective of energy saving, continuing to increase the stirring rate will also increase the cost in practical engineering applications. Therefore, it is necessary to adjust the stirring intensity according to the reactor volume, which can make the solution fully mixed, but also consider energy saving.

In addition to the limitations of the reactor configuration, the electrode spacing also affects the nitrate reduction rate. Increasing the distance between electrodes will lead to an increase in transfer impedance, resulting in unnecessary economic losses [73]. However, when the distance between the pole plates is too small, the viscous effect of the solution between them is relatively enhanced. It causes a decrease in the turbulence of the liquid between the electrode plates, which leads to a decrease in the mass transfer capacity of nitrate or other nitrogen compounds between them. Therefore, the pole plate spacing can be adjusted according to the actual reactor and electrode area [74].

5. Application in real wastewater

The electrochemical reduction of nitrate to produce ammonia with the practical wastewater was summarized in Table 1 [12,13,16,75-79]. An electrochemical nitrate reduction to ammonia system with a working volume of 500 L was used to treat the practical chemical industry wastewater, the percentage of NH_4^+–N selectivity exceeded 92.0% with concentrations ranging from 241 mg/L up to 2527 mg/L. In addition, the NH_4^+–N production rate showed no decay after 2 months of continuous operation, demonstrating the feasibility of converting nitrates in practical wastewater to value-added ammonia *via* electrochemical reduction [16]. It was reported that ammonia recovery from outflowing wastewater from the water plant with 3.47 mg/L of the nitrate nitrogen concentration by ENRA, with an ammonia production efficiency of 76.40% and nitrate removal efficiency of 99.5% in the addition of Na_2SO_4, while the nitrate removal efficiency was decreased by 39% and the ammonia yield was 1.05 mg/L after 3 h without the addition of Na_2SO_4 [77]. Firstly, ENRA can achieve high-efficiency ammonia recovery efficiency with a wide distribution of nitrate concentrations in practical wastewater. At high nitrate concentrations, the reaction rate is virtually unaffected as nitrate is far more competitive than other ions, and ammonia recovery efficiency can also be maintained at high levels ($>$ 70%) at low nitrate concentrations, but the recovery rate is not proportional to the cost of recovery in most cases. It can be achieved by concentrating the nitrate effluent to increase the ammonia yield. The concentration process undoubtedly increases the cost of the system and therefore the economic benefits of concentration and ammonia production need to be considered before the concentration process. This then leads to the question of how to obtain a high value-added ammonia product to mitigate the cost of concentration. In addition, the effect of impurity ions on the ENRA system is mentioned in Section 4.3. Ca^{2+} and Mg^{2+} in the real wastewater have the most significant impact on ammonia production efficiency and nitrate reduction rates due to their precipitation and adhesion to the electrode surface [56]. Ca^{2+} and Mg^{2+} are equivalent to hardness indicators in the field of wastewater treatment and can be removed using softening process. The current softening process with good economic effect is coagulating sedimentation (the addition of lime and Na_2CO_3 by chemical reaction and physical precipitation to remove Ca^{2+} and Mg^{2+}) [80].

6. Major challenges for large-scale applications

6.1. System structure

It is well known that the volume of the ENRA reactor varies from 30 mL to 500 mL at laboratory scale, which is far from sufficient for wastewater treatment. The main problems are the

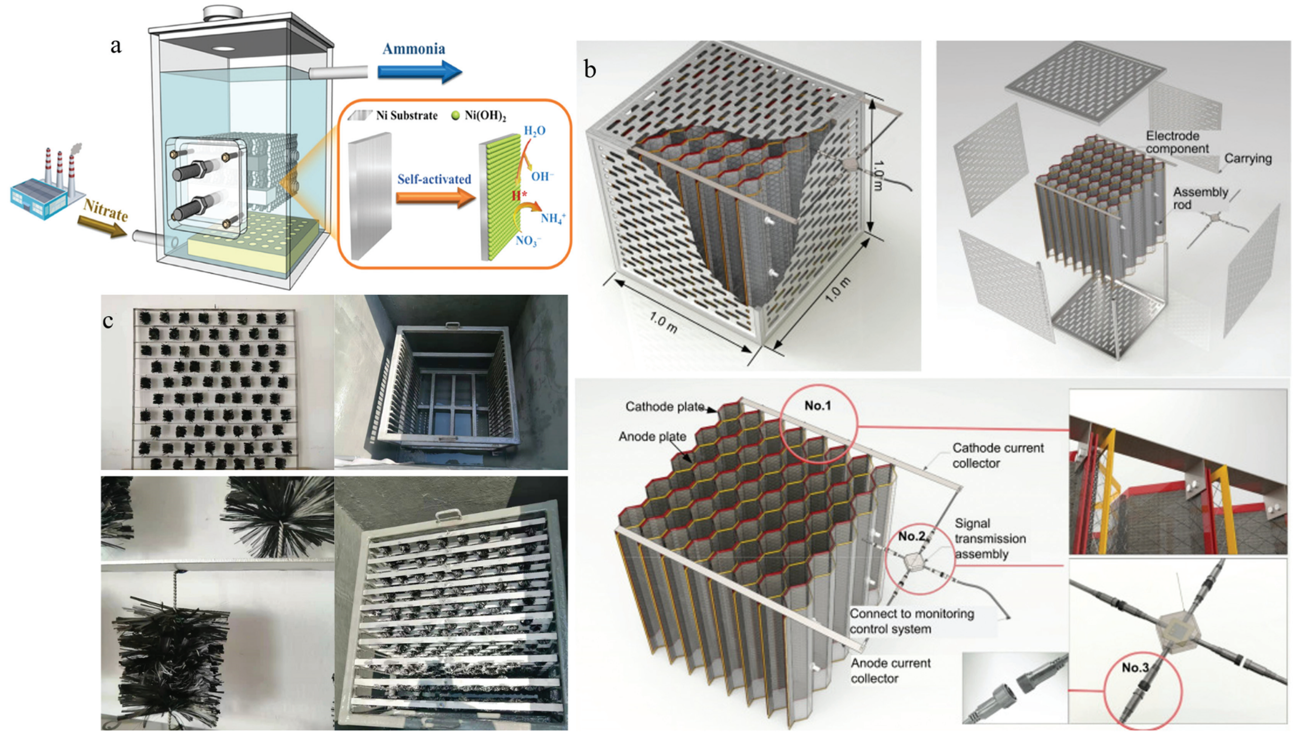

Fig. 4. Electrode module construction suitable for large scale down. (a) ENRA. Copied with permission [16]. Copyright 2021, ACS Publications. (b) Stacked electrode module (Bioelectrochemistry). Copied with permission [77]. Copyright 2020, Elsevier. (c) Sandwich-corrugated electrode module (Bioelectrochemistry).

reactor configuration and electrode design if the scale of electrochemical devices is scaled up to hundreds of liters or even cubic. The operation of industrialized devices often adopts a continuous flow state, which requires the device to have excellent hydraulic flow state and less dead zone to achieve uniform reduction of nitrates. In terms of electrode design, reasonable electrode space utilization can also improve the turbulence of wastewater to promote mass transfer between nitrate and electrodes, improving nitrate reduction efficiency and ammonia generation efficiency. On the other hand, electrode materials need to be modified to ensure catalytic sites, which makes their preparation difficult and expensive. The electrode pieces are often present individually on a laboratory scale, so if they were to be scaled up directly, not only would there be technical difficulties with the modification, but the ohmic internal resistance of the electrodes would increase dramatically.

A pilot ENRA system with a working volume of 500 L was therefore constructed (Fig. 4a), the core solution was to place two electrode stacks with 13 electrode sheets near the bottom of the reactor to form an electrode module [16]. The form of stacked electrode module was used much earlier in bioelectrochemistry. The designed electrode module with a total volume of 1 m^3 (L × W × H: 1.0 m × 1.0 m × 1.0 m) was constructed to contain eight pairs of sandwiched corrugated electrodes (cathode and anode of graphite coated stainless steel and carbon felt respectively), collector, power management system and unplasticised polyvinyl chloride cage (Fig. 4b) [81]. Similarly, our group has constructed an electrode module for pilot application (Fig. 4c), which consists of 10 sets of 1 m × 1 m carbon brush assemblies, with 5 sets of cathodes and 5 sets of anodes arranged crosswise with a controlled spacing of 10 cm. In summary, placing the electrode module assembly in the continuous flow wastewater treatment reactor can not only alleviate the difficulty of the batch reactor's limited processing capacity, but also solve the limitation of the number of reaction sites on the electrode surface. In addition, this electrode module alleviates the defect of unstable performance under the fluctuation of water quality and quantity due to its large space utilization rate. In terms of reactor configuration, perhaps strategies such as spiral tube reactors or multi-point feeds could improve the poor hydraulic flow regime.

6.2. *Economy*

Economic effect is an integral part of electrochemical reduction of nitrate to ammonia production. Mainstream ammonia synthesis processes are summarized in Table 2 [13,78,79,82-88]. The current mainstream ammonia synthesis process is HB, electrochemical nitrogen reduction reaction and ENRA. In general, HB process, as one of the greatest achievements in the 20th century, cannot deny the economic effect it brings to human beings. But in terms of current national ideas and capital investment, the HB process is unsustainable. On the other hand, NRR is less efficient in overall ammonia production due to its poor nitrogen solubility and high inertness, not to mention the primary competition (HER) that easily occurs on most catalysts. The economic effect of ENRA is particularly significant. First, ENRA can be applied to the treatment of nitrate brine to realize the concept of turning waste into treasure. Secondly, nitrate is widely present in biological treatment tail water, which lays the foundation for its application. Third, the construction of the pilot ENRA system broke through the laboratory barriers. A more detailed economic assessment will be referred to below. Economic indicators involved in ENRA are electrical energy output, electrode cost and ammonia product return. It was found that the cost-effectiveness ratio of electric energy-driven ENRA in neutral medium was 0.45 (input to output ratio) without considering the cost of cathode materials (BCN@Ni). At this time, the faradaic efficiency of ammonia was only 59.2%, which makes it difficult for the subsequent extraction of ammonia products [76]. Another study, the cost-effectiveness ratio and faradaic efficiency of the electrical-driven ENRA were 0.498% and 82.68% without considering the cost of $Pd_{10}Cu/BCN$ as cathode materials [13].

Table 2
Mainstream ammonia synthesis process.

Process	Catalyst	Parameters	Conversion efficiency	Ref.
Haber-Bosch	20% Fe–BaH$_2$ (chemical looping synthesis)	Reactor temperature: 400 °C Reactor pressure: 0.9 MPa WHSV: 60 000 mL g^{-1} h^{-1}	NH$_3$ synthesis rate: 1703 μmol g^{-1} h^{-1}	[82]
Haber-Bosch	Ni$_2$Mo$_3$N	Reactor temperature: 400 °C Reactor pressure: 0.1 MPa WHSV: 9000 mL g^{-1} h^{-1}	NH$_3$ synthesis rate: 395 μmol g^{-1} h^{-1}	[83]
Haber-Bosch	4.7% Co/BaLa$_2$O$_3$−xHyNz	Reactor temperature: 350 °C Reactor pressure: 1.0 MPa WHSV: 36000 mL g^{-1} h^{-1}	NH$_3$ synthesis rate: 19.3 mmol h^{-1} g^{-1}	[84]
ENRR	Fe-doped SnO$_2$	Electrolyte: 0.1 mol/L HCl Electric potential: −0.3 V *vs.* RHE	Ammonia yield rate: 82.7 μg h^{-1} mg$_{cat}$$^{-1}$	[85]
ENRR	V-doped TiO$_2$	Electrolyte: 0.5 mol/L LiClO$_4$ Electric potential: −0.5 V *vs.* RHE	Ammonia yield rate: 17.73 μg h^{-1} mg$_{cat}$$^{-1}$	[86]
ENRR	ZIF-derived nitrogen-doped nanoporous carbon	Electrolyte: 0.1 mol/L KOH Electric potential: −0.3 V *vs.* RHE	Ammonia yield rate: 9.22 mmol g^{-1} h^{-1}	[87]
ENRR	N-doped porous carbon (NPC)	Electrolyte: 0.05 mol/L H$_2$SO$_4$ Electric potential: −0.9 V *vs.* RHE	Ammonia yield rate: 1.40 mmol g^{-1} h^{-1}	[88]
ENRA	Pd$_{10}$Cu/BCN	Nitrate concentration: 100 mmol/L NO$_3$$^-$ Electric potential: −0.6 V *vs.* RHE	Ammonia yield rate: 31154 μg h^{-1} mg$_{cat}$$^{-1}$ Faradaic efficiency: 82.68% Cost-effectiveness ratio: 0.498	[13]
ENRA	BCN@Ni	Nitrate concentration: 100 mmol/L NO$_3$$^-$ Electric potential: −0.4 V *vs.* RHE pH ≈ 7	Ammonia yield rate: 801.0 μg h^{-1} cm^{-2} Faradaic efficiency: 59.20% Cost-effectiveness ratio: 0.45	[78]
ENRA	OP-CoP	Nitrate concentration: 208 mg/L NO$_3$$^-$-N Applied voltage: 7 V	Ammonia recovery rate: 103 g NH$_3$-N m^{-2} day^{-1}	[79]

Notes: WHSV (weight hourly space velocity); ENRR (electrochemical nitrogen reduction reaction).

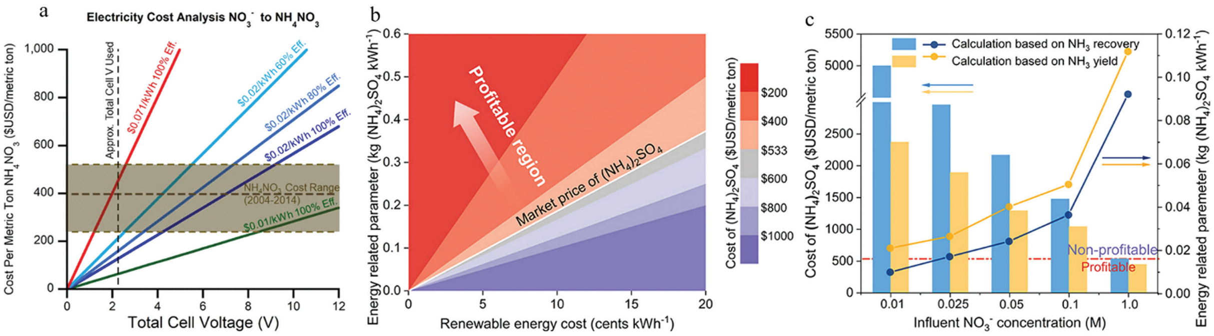

Fig. 5. (a) The economic cost of electroreduction of nitrate to NH$_4$NO$_3$ based on a given price of electricity, cell efficiency, and total cell potential applied. Copied with permission [30]. Copyright 2021, ACS Publications. (b) The profitable area of power output and energy efficiency functions (energy-related parameters determined by NH$_3$ recovery/yield as a function of electricity cost) based on the ammonia recovery product as (NH$_4$)$_2$SO$_4$. Copied with permission [79]. Copyright 2021, ACS Publications. (c) Energy-related parameters and corresponding electrical energy costs as a function of different nitrate concentrations. Copied with permission [79]. Copyright 2021, ACS Publications.

Therefore, it was understandable to sacrifice cost-effectiveness in order to obtain high value-added or high-yield ammonia. High value-added ammonia often exists in the form of fertilizers such as NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$, Fig. 5a demonstrated the economic cost of electroreduction of nitrate to NH$_4$NO$_3$ based on a given price of electricity, cell efficiency, and total cell potential applied. The results show that it was feasible to obtain NH$_4$NO$_3$ with ENRA technology at low electricity costs and reasonable Faradaic efficiencies [30]. Fig. 5b showed the profitable area of power output and energy efficiency functions (energy-related parameters determined by NH$_3$ recovery/yield as a function of electricity cost) based on the ammonia recovery product as (NH$_4$)$_2$SO$_4$. Furthermore, evaluating its system economics in terms of energy-related parameters and corresponding electrical energy costs as a function of different nitrate concentrations, ENRA was found to be profitable only at high concentrations of nitrate (1 mol/L) (Fig. 5c) [75]. This series of economic indicators does not even take into account the cost of electrode materials, system maintenance costs, separation and concentration costs. It will undoubtedly bring predictable resistance to its large-scale application. Of course, there are also feasible methods: (1) Take the membrane concentrate as the treatment object. The membrane concentrate is the residue of the wastewater retained by the reverse osmosis or nanofiltration membranes, and the pollutants are mainly dissolved organic matter and a large number of inorganic ions. The low nitrate wastewater is also enriched with nitrate after retention, thus obtaining high nitrate wastewater. Of course, the concentration of other unhelpful pollutants will have adverse effects on the ENRA system, so when designing the treatment process, the arrangement of each treatment unit is particularly important; (2) Select the electrode materials that have been industrialized. In order to promote the large-scale application of ENRA, the economic benefits of the catalyst as the core of its reaction still need to be considered. Cu has been widely recognized as the catalyst with the highest activity for nitrate reduction and ammonia production [3], and the main component of brass mesh (5.7–22.9 \$/m^2) is copper (65%), which is undoubtedly a base material with great potential for industrialization. And the catalyst to be deposited can choose non-precious metal or non-metallic (Cu, Bi, Co, C, Ni, *etc.*) to further reduce the cost [22,89,90]. However, the economic

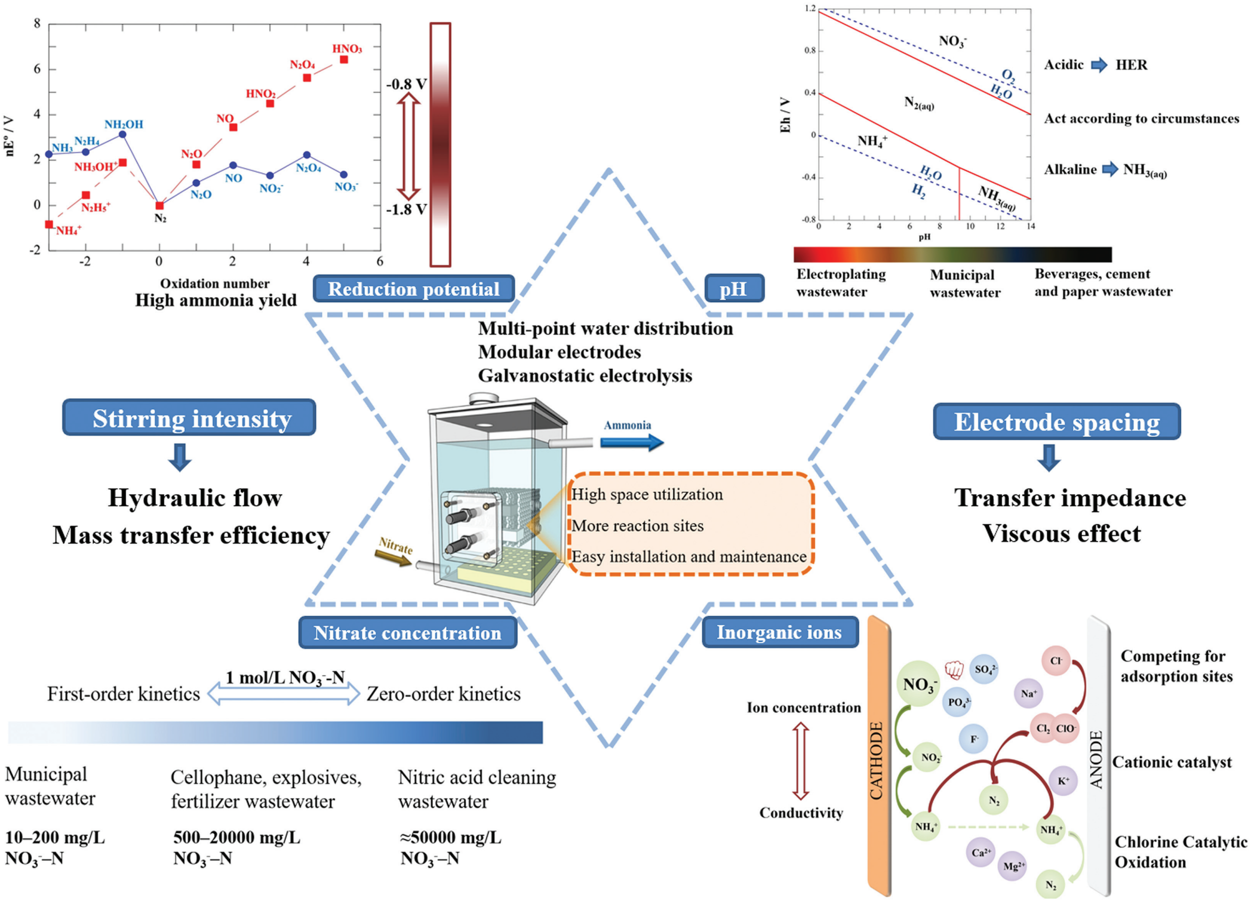

Fig. 6. Regulation strategy and system construction of ENRA under large-scale application.

effect of industrializing electrode materials or catalysts is not only reflected in the cost of the material, but also how to scale up and the long-term stability of the material. The expansion strategy has been mentioned in Section 6.1. The long-term stability of materials needs to be tested in actual engineering, carbon materials and BDD have application potential [91,92]. In practical applications, the replacement cycle, material cost, and comprehensive evaluation of ammonia production efficiency should be combined; (3) Optimize the system parameters to balance the power output and the value of the ammonia product (The details of the optimization parameters have been described in Sections 4 and 5).

7. Conclusions and prospects

The ENRA process provided a win-win strategy for nitrate removal and ammonia recovery. At present, the majority of study focus on the material perspective, rarely deals with operational control. Therefore, the mechanism of ENRA, the construction of the reaction system, the operation control strategies, the application in practical wastewater and the challenges that still need to be faced were reviewed (Fig. 6). Although studies have been conducted to apply ENRA to practical wastewater treatment at pilot scale, there are still many technical gaps that need to be addressed.

(1) Realizing the recovery of ammonia from practical wastewater is one of the most important conditions for the large-scale application of ENRA technology. Most of the existing ENRA studies focus on artificial wastewater, which only contains nitrates and electrolytes, while the species and concentration of ions in practical wastewater are more complex and related to electrical conductivity. In theory, the oxidation/reduction potentials of some ions are lower than the voltage applied to the nitrate reduction reaction, resulting in more side reactions. In addition, the conductivity of wastewater will directly affect the supply of applied voltage. In the case of high resistance, the voltage demand value will be high, resulting in significant increase in operating costs. On the other hand, organic pollutants in actual wastewater also make it difficult to remove nitrate and generate ammonia. Due to organic pollutants also have the ability to be oxidized or reduced, and the reduction reaction of nitrate will inevitably be accompanied by the reduction of organics (azo dyes, halogenated hydrocarbons, *etc.*), resulting in the loss of electrons and reduction of faradaic efficiency. And the organic oxidation reaction of the anode can replace the traditional anode reaction (water electrolysis). In order to realize the efficient and economical operation of ENRA technology in future research. The threshold value of impurity ion concentration still needs to be determined, and the existence of organics requires in-depth evaluation of the various economic benefits of this technology due to both advantages and disadvantages.

(2) Clarifying the device and electrode matching degree of ENRA technology can provide a guarantee for large-scale application. The devices of laboratory-scale ENRA were mostly dual-chamber systems with ion-exchange membranes and electrode areas on the centimeter scale, which leads to the difficulty of device construction and how to expand the electrode. First of all, if the traditional double-chamber device is scaled up, it will lead to a sharp increase in the cost of the membrane and the difficulty of flexible operation. Although the relative direct amplification single system can solve the above shortcomings, the problems of poor hydraulic flow and high dead

zone rate will appear. Furthermore, the electrode module provides a potential approach for the deletion of single electrode catalytic sites. Therefore, future research can focus on integration with wastewater treatment equipment. For example, the construction can simulate an anaerobic up-flow sludge bed system (UASB) to achieve homogeneous removal of nitrate and stable recovery of ammonia. In addition, the combination with the anaerobic baffled reactor (ABR) and the internal circulation reactor can not only achieve a dead zone rate of less than 5%, but also establish two or even multiple sets of ENRA systems with electrode module in series. Of course, how to efficiently match the coupling device and achieve stable operation still needs to be discussed.

(3) Building the efficient system is essential to recover ammonia/ammonium in electrochemical nitrate reduction from wastewater for processing into products. In the past, most of the ENRA research process has stayed at the realization of high selectivity or high faradaic efficiency of ammonia, but neglected the recovery of ammonium/ammonia to achieve real resource recovery. The key issues are mainly concentrated on ammonium/ammonia concentration and recovery methods. In theory, most recovery methods can achieve perfect recovery of low-concentration ammonia, while the cost value paid is too large, resulting in an imbalance of cost-effectiveness. Therefore, wastewater concentration is a major precondition for ammonium/ammonia recovery (limited to ammonia concentration less than 10 mg/L). At present, ammonia recovery methods mainly include regenerated resins method, membrane stripping, *etc.* It is most important to adapt the treatment according to the wastewater type to maximize the economic benefits of ammonia/ammonium recovery. In general, the ammonium/ammonia concentration of the recovered target needs to be determined first and whether required for concentrated pre-treatment, and then each recovery process needs to be selected based on the type of wastewater to obtain the most economically efficient methods.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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