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REVIEW ARTICLE

Electrochemical removal of nitrate in industrial wastewater

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HIGHLIGHTS

- Electrochemical removal is promising in nitrate elimination from wastewater.
- Influencing factors of nitrate electrochemical removal are critically reviewed.
- Electroreduction pathways of nitrate undergo electron transfer and hydrogenation.
- Electrocoagulation pathways of nitrate undergo coagulation, reduction, flotation.
- Electrodialysis pathways of nitrate undergo dialysis, reduction and oxidation.

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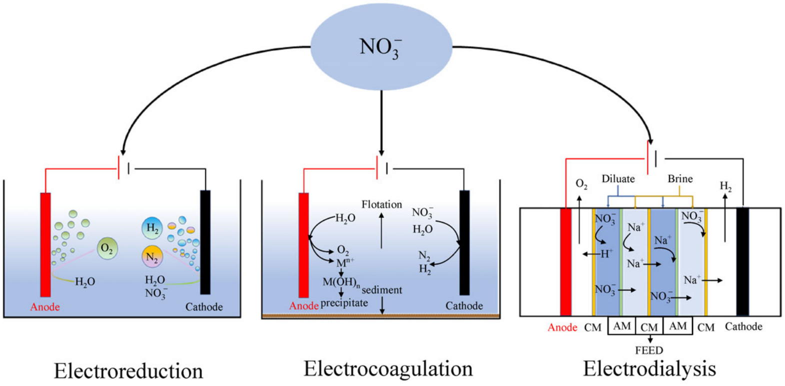
GRAPHIC ABSTRACT



ABSTRACT

A number of recent studies have demonstrated that electrochemical technologies, including electroreduction (ER), electrocoagulation (EC), and electrodialysis (ED), are effective in nitrate elimination in wastewater due to their high reactivity. To obtain the maximal elimination efficiency and current efficiency, many researchers have conducted experiments to investigate the optimal conditions (i.e., potential, current density, pH value, plate distance, initial nitrate concentration, electrolyte, and other factors) for nitrate elimination. The mechanism of ER, EC and ED for nitrate removal has been fully elucidated. The ER mechanism of nitrate undergoes electron transfer and hydrogenation reduction. The EC pathways of nitrate removal include reduction, coagulation and flotation. The ED pathways of nitrate include redox reaction and dialysis. Although the electrochemical technology can remove nitrate from wastewater efficiently, many problems (such as relatively low selectivity toward nitrogen, sludge production and brine generation) still hinder electrochemical treatment implementation. This paper critically presents an overview of the current state-of-the-art of electrochemical denitrification to enhance the removal efficiency and overcome the shortages, and will significantly improve the understanding of the detailed processes and mechanisms of nitrate removal by electrochemical treatment and provide useful information to scientific research and actual practice.

1 Introduction

Wastewater containing high concentration of nitrate has caused eutrophication in natural water in recent years. Nitrate can cause toxic effect toward humans due to its reduction to nitrite, which can be transformed into the precursor of carcinogenic nitrous amine [1]. This may result in methemoglobinemia, also known as “blue baby syndrome”. Therefore, efficient denitrification technology is urgent to be developed for the remediation of nitrate-containing wastewater [2–4].

Various technologies have been developed to remove

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nitrate from wastewater [5–11]: 1) biological denitrification, 2) physical removal, and 3) chemical reduction. In biological denitrification process, nitrate can be reduced by enzymatic reduction function of microorganisms in the presence of organic or inorganic reducing agents [12–15]. Biological denitrification is the most effective and cheapest method for treatment of nitrate-containing wastewater. This technique is applicable to all wastewater so long as bacteria grow well. But the unstable quality and quantity of industrial wastewater greatly affect the microbial activity. Therefore, the biological denitrification technique is not competitive against other processes for nitrate removal from industrial wastewater. Another drawback of biological denitrification technique is sludge generation, which requires post-treatment with high cost [16,17].

Among the physical removal methods, reverse osmosis and ion exchange are the most widely applied treatment methods for nitrate removal [18]. These methods displace nitrate but do not destroy ions from wastewater with concentrated nitrate brine generation. The generated nitrate-containing wastewater needs to be treated and disposed with high costs [19]. In summary, physical technology is a fast method for nitrate removal. Disposal technologies with low economic cost and high regeneration efficiency should be developed to treat nitrate saturated brine, and these shortcomings limit implementation of the physical removal methods [20].

Chemical reduction has been recognized as a promising technology for nitrate removal. The biggest advantage of this technology is the reduction of nitrate to non-toxic nitrogen [21–23]. Among chemical technologies, electrochemical removal has been considered as an alternative treatment to other chemical denitrification methods, such as active metal reduction and catalytic hydrogenation reduction methods [24–27]. The main advantages of the electrochemical methods are their simplicity, no production of sludge and no need for continuous maintenance or chemical reagents [28–30].

Electrochemical denitrification methods mainly include electroreduction (ER), electrocoagulation (EC), and electrodialysis (ED) techniques. They are three typical electrochemical methods for nitrate removal. ER and EC can reduce nitrate to nontoxic nitrogen while ED mainly involves physical processes such as adsorption and migration. ER technique is applicable for high salinity wastewater due to high nitrate removal efficiency and no fouling or scaling generation. EC technique can be used for wastewater recycling with great separation of nitrated floc from water. ED technique is efficient for drink water treatment. In this work, we presented a general review on the application of ER, EC and ED techniques to eliminate nitrate from wastewater. The reaction mechanism for each technique has been summarized. In addition, to obtain the optimal operation conditions for removal of nitrate in wastewater, we summarized the factors (such as electrode, pH, and potential) affecting the electrochemical denitrification efficiency. Finally, the positive and negative aspects for each technology were analyzed and compared.

2 Electroreduction technique

The electroreduction technique has been applied to transform nitrate to harmless nitrogen from wastewater in past few decades due to its high efficiency and ambient operating conditions. For example, textile industry wastewater has been treated by the electroreduction process and 85% nitrate has been removed by using Co_3O_4/Ti with Ir-Ru/Ti electrodes after 3 h [31]. The synthetic aquaculture wastewater has been treated over graphite and TiO_2 electrodes at pH 7 and a constant current of 1.5 A, and about 99% nitrate has been eliminated [32]. The reaction mechanism depends strongly on the type of cathode material, cathode potential, and solution pH. The products of nitrate electroreduction mainly include nitrogen, nitrite, and ammonium [33–36]. The selective reduction of nitrate to nitrogen is desired during electroreduction process. To improve the performance and selectivity toward nitrogen of nitrate electroreduction technology, the elimination mechanism and influence factors of electroreduction technique have been wildly investigated.

2.1 Mechanism

To improve the reaction rate for electrochemical denitrification technology, researchers have studied the mechanism of nitrate removal on cathode for many years. Nitrate reduction mechanism can be explained by two fundamental pathways: (I) involving electrons [34,37,38]; (II) involving hydrogen atoms [39], as shown in Fig. 1.

The eliminate pathway of nitrate (I) [40,41]:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-,\ E_0 = 0.01\ \text{V} \quad (1)$$

$$NO_3^- + 3H_2O + 5e^- \rightarrow 0.5N_2 + 6OH^-,\ E_0 = 0.26\ \text{V} \quad (2)$$

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-,\ E_0 = -0.12\ \text{V} \quad (3)$$

$$NO_3^- + 2H_2O + 3e^- \rightarrow 0.5N_2 + 4OH^-,\ E_0 = -0.406\ \text{V} \quad (4)$$

$$NO_3^- + 5H_2O + 6e^- \rightarrow NH_3 + 7OH^-, E_0 = -0.165\ \text{V} \quad (5)$$

$$NO_3^- + 4H_2O + 4e^- \rightarrow NH_2OH + 5OH^-, E_0 = -0.45\ \text{V} \quad (6)$$

According to mechanism (I), nitrate is catalyzed by electrons and the reaction occurs on the cathode surface, where nitrite, nitrogen, ammonium and other redox products can be involved. Nitrate reduction to nitrite has

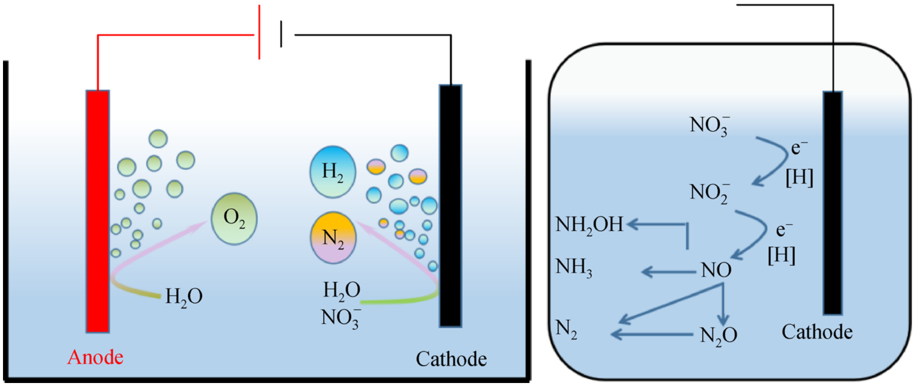

Fig. 1 Proposed mechanism of electrochemical denitrification technology

been recognized as the rate-limiting step of the whole process [38]. And ammonium may constitute the main final product.

The elimination pathway of nitrate (II) [42]:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{7}$$

$$H_2 + 2M[\ ] \rightarrow 2M[H] \tag{8}$$

$$NO_3^- + M[H] \rightarrow M[NO_2] + OH^- \tag{9}$$

$$M[NO_2^-] + M[H] \rightarrow M[NO] + OH^- \tag{10}$$

$$M[NO] + M[\ ] \rightarrow M[N] + M[O] \tag{11}$$

$$M[N] + M[N] \rightarrow 2M[\ ] + N_2 \tag{12}$$

$$M[NH] + M[H] \leftrightarrow M[NH_2] + M[\ ] \tag{13}$$

$$M[NH_2] + M[H] \rightarrow M[NH_3] + M[\ ] \tag{14}$$

$$M[NH_3] \rightarrow NH_3 + M[\ ] \tag{15}$$

According to mechanism (II), the reactions start with the adsorption of H_2O (Eq. (7)) and nitrate (Eq. (9)) onto the electrode and quickly reach dynamic equilibrium. When a constant current is applied on the electrode surface, the adsorbed H_2O can be reduced to the absorbed hydrogen atoms (M[H]). The reaction between the M[H] and adsorbed nitrate has been recognized as the rate-determining step in the reduction process [39]. As a result, [H] plays a primary role in the whole process of electrocatalytic reduction of nitrate.

The nitrate electroreduction mechanism is different with different electrodes. For example, mechanism (II) is more likely to occur when Pt, Rh, Ni are used as cathode, the outer electron structure with empty d orbit of those metals attributes to hydrogen atoms adsorption, forming M[H] [43]. The nitrate reduction reaction on Cu electrode mainly follows the mechanism (I), because Cu electrode has a strong adsorption capacity for nitrate [41].

The desired cathodic process is reduction of nitrate to nitrogen, but the reaction mechanism in the electroreduction of nitrate principally depends on the cathode material, applied potential, pH of the aqueous solution, and other anions.

2.2 Influence factors on electroreduction efficiency of nitrate in wastewater

2.2.1 Electrode material

Electrode material is essential for electrochemical reduction system, and directly affects the reaction rate of pollutants [45,46]. Many cathodes have been developed for nitrate electroreduction. Table 1 summarizes the researches into the electroreduction of nitrate by various cathode materials. It can be seen that the electrode material is mainly divided into non-metallic electrode and metal electrode. Boron doped diamond (BDD) electrode and graphite are two typical nonmetallic cathodes. BDD electrode has been considered as the most powerful electrode for pollutant reduction [46–48]. The treatment of slaughterhouse wastewater has been performed on BDD as anode/cathode with an applied current density of 35.7 mA/cm^2 without reagent. Nitrate was removed completely after 180 min, and nitrogen was the main products [49]. However, the industrial application of BDD electrode is limited due to expensive price and lack of suitable substrates [50]. Graphite has also been used as cathode for the electrochemical reduction of nitrate. The reduction rate was very low (8%) when pure graphite was used as cathode. Therefore, modified graphite electrode has been studied to improve the removal rate for nitrate. Previous researchers have selected Rh-graphite electrode as cathode to remove nitrate from wastewater [51–53], about 60% of NO_3^- was reduced after 96 h, and ammonium was the main product. The low reduction rate and selectivity for nitrogen has limited the application of Rh-modified graphite electrode.

Table 1 Summary of nitrate electroreduction over different types of cathodes

Cathode	Nitrate concentration (mg/L)	Electrolyte (mg/L)	Other parameters	$X_{NO_3^-}$ (%)	k* (min^{-1})	S_{N_2} (%)	Onset potential (V)	Ref
Graphite felt	170	NM*	Constant voltage: -1.8 V 2 h	70	NM*	NM*	-0.8	[66]
Pt	4250	3725 (KCl)	180 min	31.2	1.5×10^{-3}	13.5	NM*	[67]
Fe	100	500 (Na_2SO_4)	NM*	93	NM*	NM*	NM*	[68]
Fe	100	500 (Na_2SO_4) 500 (NaCl)	NM*	87	NM*	87	NM*	[68]
Fe	50	500 (Na_2SO_4)	NM*	91	NM*	NM*	NM*	[68]
Fe	50	500 (Na_2SO_4) 500 (NaCl)	NM*	94.3	NM*	NM*	NM*	[68]
Ti	170	NM*	Constant voltage: -1.8 V 2 h	8	NM*	NM*	-1.0	[66]
Co_3O_4/Ti	100	71000 (Na_2SO_4)	NM*	65	NM*	NM*	NM*	[31]
Co_3O_4/Ti	100	71000 (Na_2SO_4) 1500 (NaCl)	NM*	96	NM*	NM*	NM*	[31]
Si/BDD	9.74	NM*	35.7 mA/cm^2 180 min	100	NM*	NM*	NM*	[48]
Cu/graphite	85000	58500 (NaCl)	NM*	NM*	1.25×10^{-6}	NM*	-0.9	[65]
Pd-Cu/graphite	85000	40000 (NaOH)	NM*	NM*	3.73×10^{-6}	90	-0.7	[65]
Cu/Pt	4250	3725 (KCl)	180 min	66	4.88×10^{-4}	12	NM*	[67]
Cu-Ni	170	NM*	Constant voltage: -1.8 V 2 h	58	NM*	NM*	-1.3	[66]
Sn-Cu/Pt	5250	3725 (KCl)	180 min	99	4.96×10^{-4}	93.8	NM*	[66]

Notes: NM* means not mentioned; k* means reaction rate constant; $X_{NO_3^-}$ means selectivity toward nitrogen

Therefore, metal electrode with low resistance and high activity has been wildly investigated for nitrate electroreduction in wastewater. Sn electrode is an attractive cathode material for nitrate removal due to its good electrical conductivity, high reduction rate and selectivity toward nitrogen [54]. Previous study has demonstrated that the removal rate of nitrate (100 mg/L) over Sn cathode was 95% and the selectivity to nitrogen reached 70% [55]. But the corrosion of Sn has been observed during reduction process. Hence, researchers usually combined Sn with Pt, Pd to remove nitrate in wastewater. In the case of Pd/Sn and Pt/Sn, Pd or Pt prevents Sn from corrosion, and Sn acts as a promoter for nitrate reduction [56,57]. Cu electrode is a promising cathode for nitrate electroreduction with low resistance and high selectivity to nitrate [58–60]. It has been reported that nitrate-to-nitrite conversion selectivity achieved 98% on Cu cathode [61,62]. The total nitrate removal rate could reach 84% when used Cu cathode, but the main problem is low nitrogen generation [63]. Therefore, researchers have focused on using modified Cu cathode to eliminate nitrate from wastewater. For example, the removal rate and nitrogen selectivity by Pd modified Cu electrode were 92% and 70%, respectively [64,65].

2.2.2 Potential

Potential is the major driving force for electroreduction of nitrate, and it significantly influences the reduction rate and products during reduction process [64]. Previous research reported that the removal rate of nitrate over Cu electrode increased from 7.5% to 22% and then 55% when the potential enhanced from –1.1 V to –1.2 V and then –1.4 V, and the ammonium selectivity increased from 13% to 39% and then 80% [40]. The different product selectivity was attributed to the different demands for electrons of products as described in Eqs. (1)–(5), which meant more negative potential favored the production of ammonium. However, when the potential was higher than a certain value, the electroreduction efficiency of nitrate decreased. When the potential enhanced from –1.8 V to –2.0 V, the electroreduction rate of nitrate over graphite cathode after 120 min electrolysis decreased from 15% to 8%, the lower efficiency was because of the strong inhibition by hydrogen evolution [66].

2.2.3 pH

The pH value of nitrate solution affects the catalytic proton-coupled electron transmission, which subsequently influences the electroreduction rate of nitrate in wastewater [69]. Previous studies have found that the electroreduction of nitrate was more favorable in acidic condition. It has been reported that there was no activity for nitrate reduction on Pt electrode when pH value was higher than 5 [70]. It can be explained by the general theory of the electrochemical reduction of nitrate. The reduction rate of nitrate increases with increasing the proton donating ability of the proton donor. It decreases in the order of $H_2O < NH_4^+ < H_3O^+$ [71]. In acidic condition, where the proton donor is the hydronium cation, the reduction rate of nitrate is expected to be proportional to the concentration of the hydronium cation.

2.2.4 Electrolyte

Supporting electrolytes are used to provide an electroconductive medium and minimize the voltage drop and resistance of electrochemical reactor [72]. The cations contributed to nitrate reduction on cathode by changing the double layer structure and forming ion pairs and brides which weakened the repulsion between anions and cathodes. This process was called “cationic catalysis” [73]. Previous studies have found that the electroreduction rate of nitrate over Sn cathode in four electrolytes increased in the trend of $Li^+ < Na^+ < K^+ < Cs^+$ [74]. The influence of cations on nitrate reduction has also been investigated. For instance, Cl^- has positive effects on the electrochemical reduction of nitrate. In the presence of Cl^-, the following reactions occur on anodes as shown in Eqs. (16)–(20) [74,75]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{16}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{17}$$

$$HClO \rightarrow OCl^- + H^+ \tag{18}$$

$$2NH_3 + 2OCl^- \rightarrow N_2 + 2HCl + 2H_2O + 2e^- \tag{19}$$

$$NO_2^- + OCl^- \rightarrow NO_3^- + Cl^- \tag{20}$$

If Cl^- is present in solution, ClO^- can be formed due to the anodic oxidation of Cl^- as shown in Eqs. (16)–(17). ClO^- can influence the products selectivity in different ways. For example, ammonium ions produced at cathode can be oxidized and transformed to nitrogen by Eq. (19), increasing the selectivity toward nitrogen. Nitrite produced by nitrate reduction on cathode can also be oxidized to nitrate by Eq. (20), thus the reduction rate of nitrate decreases. The effect of Cl^- on electroreduction of nitrate on BDD electrode has been studied [76]. Cl^- accelerated the reduction rate for nitrate, and increased the selectivity toward nitrogen. Several works about the effect of SO_4^{2-} on nitrate electroreduction has also found that SO_4^{2-} inhibited the reduction rate of nitrate due to the competition between SO_4^{2-} and NO_3^- for active sites on the surface of electrode [56].

2.2.5 Other factors

Some researchers have investigated the effect of other factors on nitrate electroreduction, such as temperature and reactor types. The nitrate removal efficiency by electroreduction over Ti cathode increased with increasing temperature because the diffusion rate and adsorption strength of nitrate increasing with higher temperature [30]. The single chamber cell (SCC) and dual-chamber cell (DCC) were the most frequently used electrocatalytic cell configurations for the electroreduction of aqueous nitrates. The SCC reactor has a unique compartment in which both electrodes are in contact with the electrolyte; in the DCC reactor, the cathodic chamber is separated from the anodic one by a cation exchange membrane. Many studies have proved that the electroreduction performance using DCC was higher than SCC, which was primarily due to the presence of the coupled catalytic reduction of nitrate with the appropriate amount of in situ generated hydrogen by electrolysis as a reducing agent [77,78].

3 Electrocoagulation technique

The electrocoagulation technique neutralizes electric charge of nitrate to remove it from wastewater based on the electrochemical production of metal ions (such as Al and Fe) that act as destabilizing agents [79–81]. Recently, many researchers have shown a great deal of interest in the electrocoagulation method as a promising alternative to remove nitrate from wastewater [82–84]. This technology electrochemically oxidizes or reduces the organic contaminants in wastewater to non-hazardous inorganic substances. The technology has potential for treating surface water, groundwater, and industrial wastewater contaminated by nitrate. Elazzouzi et al. [85] treated urban wastewater using aluminum electrode plates. At operating condition of pH 7 and current density of 2 mA/cm^2, 70% of nitrate has been removed. Molasses wastewater has been treated by this technique. Under the optimum condition of reaction time at 3.5 h, current density at 32.76 mA/cm^2 and 45% water dilution, the removal rate of nitrate was 51.72% [86].

3.1 Mechanism

Electrocoagulation is an effective technology for removal of nitrate from wastewater. Generally, the mechanism of electrocoagulation in nitrate wastewater includes three pathways, electrocoagulation, electroflotation, and electroreduction as shown in Fig. 2 [87]. Electrocoagulation is the process of destabilizing suspended, emulsified, or dis-

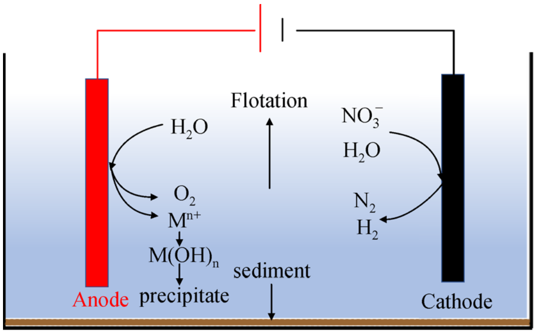

Fig. 2 Proposed mechanism of nitrate removal by electrocoagulation technology

solved nitrate in solution by introducing an electric current into the solution. The metals and metal hydroxide cations take part in the electrocoagulation process. Electroflotation is the process in which gas bubbles take pollutants to the surface. Electroreduction process involves reduction of nitrate on cathode. The anodes are usually made of aluminum and iron, and reactions occur on electrodes as shown in Eqs. (21)–(26) [88,89]:

$$3NO_3^- + 3H_2O + 2Al \rightarrow 3NO_2^- + 2Al(OH)_3 \tag{21}$$

$$3NO_3^- + 3H_2O + Al \rightarrow 3NO + Al(OH)_3 + 3OH^- \tag{22}$$

$$NO_2^- + 5H_2O + 2Al \rightarrow NH_3 + 2Al(OH)_3 + OH^- \tag{23}$$

$$2NO_2^- + 4H_2O + 2Al \rightarrow N_2 + 2Al(OH)_3 + 2OH^- \tag{24}$$

$$NO_3^- + 10H^+ + 4Fe \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \tag{25}$$

$$NO_2^- + 8H^+ + 3Fe \rightarrow 3Fe^{2+} + NH_4^+ + 2H_2O \tag{26}$$

3.2 Influence factors on electrocoagulation efficiency of nitrate in wastewater

3.2.1 Electrode material

Choice of electrode material is essential for achieving the maximum efficiency of the EC process. Various electrode materials have been used for electrocoagulation technology such as Al, Fe, Ca, Cd, Cr, Cs, Ag, Mg, Si, and Zn [90]. Table 2 summarizes the electrodes used for nitrate removal by electrocoagulation. Among them, Al and Fe electrodes are wildly used due to their coagulating properties of multivalent ions [91]. The removal rate for nitrate varied significantly among different electrodes. For example, previous researchers removed nitrate from wastewater by Al or Fe anode, and found that the removal efficiency of Al was higher than Fe after 60 min electrolysis. This was primarily because flocs generated by Al have larger coagulation capacity [87]. Some other workers found that although the nitrate removal rates of Al and Fe anode reached 80% after 60 min electrolysis, they observed that the removal efficiency of nitrate was higher

Table 2 Summary of nitrate electrocoagulation over different types of electrodes

Anode-Cathode	Current density (mA/cm^2)	Voltage (V)	pH	Electrolysis Time (min)	Nitrate concentration (mg/L)	Removal rate (%)	Ref
Mg-Mg	1	NM*	7	NM*	500	83.33	[93]
Mg-Mg	1.5	NM*	7	NM*	500	90.27	[93]
Mg-Mg	2.5	NM*	7	NM*	500	92.9	[93]
Mg-Mg	5	NM*	7	NM*	500	93.43	[93]
Mg-Mg	7.5	NM*	7	NM*	500	93.87	[93]
Al-Al	25	NM*	7	60	100	52	[87]
Al-Al	NM*	20	5	60	150	72	[92]
Al-Al	NM*	20	7	60	150	78	[92]
Al-Al	3.57	NM*	5	40	100	62.8	[94]
Al-Gr	25	NM*	7	60	100	87	[87]
Al-Fe	25	NM*	7	60	100	41	[87]
Al-Fe	3.57	NM*	5	40	100	81.5	[94]
Fe-Fe	25	NM*	7	60	100	47	[87]
Fe-Fe	3.57	NM*	5	40	100	71.2	[94]
Fe-Al	25	NM*	7	60	100	73	[87]
Fe-Gr	25	NM*	7	60	100	58	[87]
Gr-Gr	25	NM*	7	60	100	81	[87]
Gr-Al	25	NM*	7	60	100	81	[87]
Gr-Fe	25	NM*	7	60	100	80	[87]

with Fe electrode. They explained that Fe anode can produce more ferrous hydroxide flocs under the same current density with less electrons required for dissolving anode [92].

3.2.2 pH

The pH values of solutions influence the speciation of metal ions and the solubility of products formed [95,96]. Thus, solution pH influences the removal efficiency and effectiveness of EC. In the case of Al and Fe anodes, aluminum, iron cations, and hydroxides cause destabilization of colloids, effective coagulant species are formed in acidic, neutral, and slightly alkaline pH. When pH is low, the hydroxides species of dissolving aluminum and iron can not be used as the coagulating agents because they can not provide effective coagulation capacity and can not stay stable. In highly alkaline pH, $Al(OH)_4^-$ and $Fe(OH)_4^-$ ions are formed, and these ions have poor coagulation performance [97–99]. Some workers used iron and aluminum anodes for nitrate removal to investigate the effect of pH, they found that the optimum nitrate removal was achieved at pH 5, and minimum removal efficiency occurred at pH 3 at the initial nitrate concentration of 100 mg/L and electrical current of 200 mA [100].

3.2.3 Distance between electrodes

It has been reported that increasing the distance between electrodes increases electric resistance against the current flowing between anode and cathodes. As the electrode gap becomes less, the lower mixing rate of the fluid between electrodes can not provide sufficient concentration polarization layer on electrode surface [101]. These effects can increase electric potential or resistance of electrodes, diminishing the NO_3^- removal efficiency subsequently. Hashim et al. [99] used Al anodes to remove nitrate from wastewater with different distances, they found that the removal rate decreased from 57.2% to 46.8% when gap increased from 3 mm to 10 mm, while the energy consumption increased from 5 $kW\cdot h/m^3$ to 11.6 $kW\cdot h/m^3$. In conclusion, the increasing of electrode space leads to higher resistance, thicker passive layer, and lower current efficiency. Hence, the nitrate removal rate is inversely proportional to the electrode space.

3.2.4 Current density

Current density is one of the main factors that directly affects the electrocoagulation performance during electrocoagulation process. Current density directly determines coagulant dosage, bubble generation rate and strongly affects both solution mixing and mass transfer on electrode, and the amount of dissolved metal strongly depends on the quantity of electricity that passes through the electrolytic solution [102]. Increasing current density can improve nitrate removal rate. But with the increasing of current density, the passivation and polarization of the electrode will be intensified, causing high energy consumption [90]. Previous studies used Al anode to remove nitrate from wastewater and observed that higher current accelerated nitrate removal efficiency, because more coagulating agents were released at higher current density. When Fe was used as anode to remove nitrate from wastewater, similar conclusion has been obtained. They found that with the current density increased from 0.16 to 1.68 A/m^2, the nitrate removal rate increased. The maximum removal rate of nitrate can reach 46.7% [103]. However, other researchers used iron and aluminum electrodes for nitrate removal and found that current density did not affect nitrate removal efficiency when the same dose of reagent was added to the treated water. This indicated that the removal rate of nitrate only depends on the amount of dissolved metal released from the anode, however, current density could significantly affect operational costs due to increase of cell potential [104].

3.2.5 Other factors

Several workers have focused on investigating the effect of other factors on nitrate removal by electrocoagulation, such as temperature and turbidity. For example, the removal rate of nitrate by electrocoagulation on Mg electrode increased with increasing temperature due to the higher mass transfer rate of nitrate [93]. The presence of colloidal particles with negative charge inhibited the removal rate of nitrate because the turbidity compete with nitrate for collision with surface sites of flocs [94].

4 Electrodialysis

Electrodialysis is a membrane process with high reliability and treatment efficiency. This technique has been mainly applied for the treatment of brackish water desalination. The electrodialysis technique is also used for the process of demineralization and deacidification in the food processing industry. Compared with reverse osmosis, electrodialysis is less sensitive to membrane fouling and scaling, leading to higher recovery rates and less brine disposal problem. The electrodialysis technique has the advantages of high selectivity and low chemical demands. This technique has been reported as one of the best separation processes for the selective removal of nitrate from water, and many electrodialysis processes have been installed for nitrate removal worldwide [105]. When electrodialysis is applied to brackish water desalination, a large fraction (typically 80%–95%) of the brackish feed is recovered as product water. Currently, some regions such as Oklahoma, Arizona use electrolysis for the treatment of brackish water and groundwater. Recently, many electrodialysis plants have been implemented specifically for the removal of nitrate from drinking water. In Israel, a plant of GE reduces the levels of nitrate from 100 mg/L to 45 mg/L. In Kazusa, Japan, the technique has been installed to reduce nitrate levels from 80 mg/L to 27 mg/L. In Bermuda, a plant removes 86% of nitrate from wastewater by electrodialysis technique.

4.1 Mechanism

Electrodialysis is a process that uses selectively permeable membranes to segregate charged species. Membranes that are permeable to either cations or anions can be modified by affixing either negatively or positively charged groups to a polymer substrate. When cation and anion permeable membranes are alternately stacked and separated by water-filled spacers, with an electrode at either end of the stack, a voltage difference between the electrodes will cause cations to move toward the cathode and anions to move toward the anode, in the case of nitrated wastewater, the electrolysis is usually carried out with a nitrate selective membrane (Fig. 3) [106]. Electrolysis reactions at the two electrodes produce gases, primarily oxygen and hydrogen, which are carried off in a recirculating stream and released to the atmosphere.

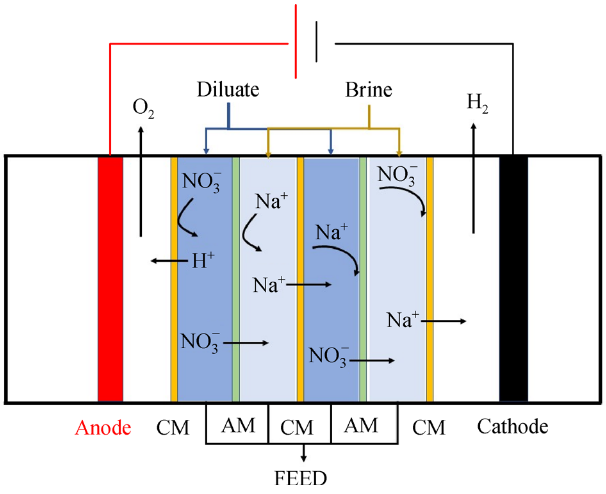

Fig. 3 Proposed mechanism of nitrate removal by electrodialysis technology

4.2 Influence factors on electrodialysis efficiency of nitrate in wastewater

4.2.1 Ion exchange membrane

The electrodialysis removal efficiency of nitrate has been demonstrated to be strongly dependent on the ion exchange membrane. Previous researchers have studied the nitrate removal on different anion exchange membranes. Table 3 summarizes the anion exchange membranes for nitrate removal by electrodialysis. It can be seen that nitrate separation rate from feed is high by electrolysis. And an ideal anion exchange membrane should have both high transport number and selectivity for counter ions. To enhance the selectivity toward nitrate, several methods have been development. For example, increase the hydrophobic nature of membrane by introducing specific anion exchange groups in the membranes [107]. The hydrophobic nature of membranes has been modified by benzyl trimethylammonium, benzyl triethylammonium, benzyl tri-n-propylammonium, or benzyl tri-n-butylammonium anion exchange groups, and the ion exchange equilibrium constant between nitrate and chloride increased with increasing carbon number of alkyl groups bounded to ammonium groups [108]. It can be concluded that as the anion exchange becomes more hydrophobic, the selectivity toward nitrate gets higher. This is primarily because the affinity of anions toward membranes depends

Table 3 Summary of ion exchange membranes for nitrate removal by electrolysis

Anion exchange membrane	Cation exchange membrane	Current density (mA/cm^2)	Voltage (V)	Time (min)	Flow rate (L/min)	Initial concentration (mg/L)	Nitrate removal (%)	P*	K*	Ref
AFN	CMX	10	NM*	60	NM*	500	80.5	NM*	NM*	[109]
ACS	CMX	10	NM*	60	NM*	500	77.5	NM*	NM*	[109]
ACS	CMX	NM*	15	10	NM*	89.69	82.64	NM*	NM*	[110]
AMX	CMX	10	NM*	60	NM*	500	75.0	NM*	NM*	[109]
AMX	CMX	NM*	10	NM*	1.6	450	96	NM*	NM*	[111]
ADP	CMX	10	NM*	60	NM*	500	76.0	NM*	NM*	[109]
ADS	CMX	10	NM*	60	NM*	500	78.9	NM*	NM*	[109]
AMI	PC-SK	NM*	5	120	NM*	850	NM*	1.79	NM*	[112]
NEOSEPTA AM1	NEOSEPTA CM-2	1.0	NM*	60	NM*	NM*	NM*	2	3.63	[113]
Py-Fe NEOSEPTA AM1	NEOSEPTA CM-2	1.0	NM*	60	NM*	NM*	NM*	5	4.84	[113]

Notes: P* means the transport number between nitrate and chloride; K* means he ion exchange equilibrium constant between nitrate and chloride on their hydration energies. The selectivity toward nitrate, a less hydrated anion, can be enhanced by developing more hydrophobic anion exchange membranes [107].

4.2.2 Operating voltage

Operating voltage is a major driving force for electrodialysis separation of nitrate, and it significantly influencs the nitrate removal efficiency. Previous researches have demonstrated that high removal that of nitrate is obtained as the potential increases [109]. The nitrate removal efficiency on ACS-CMX ion exchange membranes increased from 61.77% to 86.65%, and then 92.52% when the potential was enhanced from 5 V to 10 V, and then 15 V [110], respectively, at flow rate of 180 L/h. It can be concluded that more ions can be transferred through the membrane at higher voltage. This is primarily because higher voltage leads to high conductivity, which facilitates ions migration. However, when the voltage was higher than a certain value, the electrodialysis rate for nitrate removal decreased. Liu et al. has reported that when the voltage was higher than 7 V, nitrate removal efficiency decreased at flow rate of 8 L/min. This was primarily because water dissociation limited the ions migration [114]. Hence, it is of great significance to choose suitable voltage for nitrate removal in practical application.

4.2.3 Flow rate

The flow rates and the applied high voltages are responsible for occurrence of concentration polarization owing to the existence of boundary layers near the membrane surfaces. Previous works have found that the electrodialysis efficiency of nitrate increased with increasing the flow rate of feed. When the flow rate increased from 100 L/h to 180 L/h, the removal rate of nitrate increased from 78.64% to 86.51% over ACS-CXM ion exchange membrane, respectively, at a constant voltage of 10 V [110]. This is due to the decrease in the thickness of the boundary layers adjacent to the membrane surfaces (static zones of solutions) with increasing solution velocity. And the thicker boundary layers was attributed to ions transportation.

4.2.4 Temperature

Temperature is an important parameter during electrolysis of nitrate in water, because the temperature influences water content of the anion exchange membrane and the ion transport number. Many researches have demonstrated that the electrolysis efficiency of nitrate increased with increasing temperature. When the temperature increased from 15°C to 25°C and 40°C, the nitrate removal rate increased from 72.97% to 76.59% and 82.64%, with a constant voltage of 15 V, respectively [110]. The increase in the removal efficiency of nitrate with temperature is due to the increase in the ion mobility and the dilation of the membrane which attributed to the membrane swelling and the diffusion of ions into membrane. On the other hand, for anion membranes, which are modified by introducing specific anion exchange groups, the increasing temperature changes the component of the anion exchange membrane, influencing the hydrophobic nature of the membrane, which affects the affinity of nitrate toward anion exchange membrane. In the case of anion exchange membrane with N-isopropylacrylamide, when the temperature increased, the transport number of nitrate increased. It can be attributed to the more hydrophobic nature of the membrane with higher temperature [107].

4.2.5 Other factors

Several researches have focused on studying the effect of other factors on the electrodialysis efficiency of nitrate, such as the initial nitrate concentration and pH of solution. It has been reported that increasing nitrate concentration facilitates the nitrate removal by electrolysis. The nitrate removal efficiency by electrodialysis increased from 81.47% to 97.66% with initial concentration increasing from 100 mg/L to 600 mg/L [109]. This is because increasing initial nitrate concentration enhances the mobility of nitrate ions with a high ionic strength. The pH value of solution governs the distribution of ions among the charged sites on the membrane surfaces. And previous studies have found that the electrodialysis of nitrate was more favorable in acidic condition due to no competition between H^+ and nitrate. It has been reported that nitrate removal rate increased in the trend of $pH\ 5 = pH\ 4.5 < pH\ 4 = pH\ 3.5 < pH\ 3 < pH\ 2.5$ [115]. In alkali condition, both water dissolution and OH^- limit the nitrate transport, decreasing the nitrate removal efficiency.

5 Conclusions and prospects

Electrochemical denitrification has attracted increasing attention during the past decades due to the advantages such as easy operation and no chemical demands. This article reviewed three different electrochemical techniques for nitrate removal, including ER, EC, and ED techniques. Satisfactory removal efficiency can be achieved by these three techniques. However, these technologies still suffer some technical, economic, and environmental barriers that hamper their application in practice.

1) The mechanism of ER technique for nitrate reduction including electron reaction and catalytic hydrogenation. The influence factors such as cathode materials and potential have been discussed. However, low selectivity toward nitrogen is still the main drawback of the process. Improving the selectivity to nitrogen is urgently required.

High selectivity can be realized through electrode modification by noble electrode such as Pt and Pd. But the high cost for Pd and Pt modification limits the application of ED technique. Further work should be done to develop electrode with low price and high selectivity to nitrogen.

2) The mechanism of EC technique for nitrate elimination mainly involves electroflotation, electrocoagulation, and electroreduction processes. Detailed work in terms of the development of advanced electrode materials, application of different electrode types, optimal design for electrolytic reactors, energy consumption, and economy still needs to be investigated. Such technology facilitates the recycling/treatment of wastewater for producing clean water at an affordable price.

3) ED is an effective method for nitrate removal from wastewater. Different influence factors have been summarized in this paper. The main disadvantage of ED technique for nitrate removal is fouling and scaling. To solve this problem, the permeation of divalent should be decreased, which can be realized by developing nitrate selectivity anion exchange membrane. In addition, further research should be conducted to investigate the effect of coexist organic matters (such as humic acid and fluvic acid) on the removal efficiency of nitrate, which have not been fully investigated yet.

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