Electrocatalytic Reduction of Nitrate via Co3O4/Ti Cathode Prepared by Electrodeposition Paired With IrO2-RuO2 Anode

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Nitrate pollution is already a global problem, and the electrocatalytic reduction of nitrate is a promising technology for the remediation of wastewater and polluted water bodies. In this work, Co3O4/Ti electrodes were prepared by electrodeposition for the electrocatalytic reduction of nitrate. The morphology, chemical, and crystal structures of Co3O4/Ti and its catalytic activity were investigated. Then, the electrocatalytic nitrate reduction performance of Co3O4/Ti as the cathode was evaluated by monitoring the removal efficiencies of nitrate (NO3−-N) and total nitrogen (TN), generation of reduction products, current efficiency (CE), and energy consumption (EC) at different operating conditions. Under the catalysis of Co3O4/Ti, NO3− was reduced to N2 and NH4+, while no NO2− was produced. After the introduction of chloride ions and IrO2–RuO2/Ti as the anode, NH4+ was selectively oxidized to N2. The removal efficiencies of NO3−-N (at 100 mg/L) and TN after 2 h were 91.12% and 60.25%, respectively (pH 7.0; Cl− concentration, 2000 mg/L; current density, 15 mA/cm2). After 4 h of operation, NO3−-N and TN were completely removed. However, considering the EC and CE, a 2-h reaction was the most appropriate. The EC and CE were 0.10 kWh/g NO3−-N and 40.3%, respectively, and electrocatalytic performance was maintained after 10 consecutive reduction cycles (2 h each). The cathode Co3O4/Ti, which is prepared by electrodeposition, can effectively remove NO3−-N, with low EC and high CE.

Keywords: nitrate removal, electrocatalytic, Co3O4/Ti, reduction, IrO2–RuO2

1 INTRODUCTION

Nitrate (NO3−) contamination of surface water and groundwater is a global environmental problem associated with increasing populations, and its hazards have attracted much attention (Jasper et al., 2014; Khalil et al., 2016; Serio et al., 2018). The accumulation of plant nutrients such as NO3− and phosphate in water can accelerate eutrophication, a process that increases the biomass of a water body as its biological diversity decreases, for example, due to increases in invertebrates and fish. In the extreme, a state of hypoxia can exist, resulting in the loss of the aquatic ecosystems (Kubicz et al., 2018; Zhang et al., 2021). Although NO3− is chemically stable, it can be microbiologically reduced to reactive nitrite in the oral cavity and stomach, which has been linked to liver damage, methemoglobinemia, and cancer in animals (Spalding and Exner, 1993; Elmidaoui et al., 2001; Barakat et al., 2020).
Currently, microbial denitrification is widely used for the large-scale remediation of NO$_3^-$ pollution (Clauwaert et al., 2007; Della Rocca and Belgiorno V Meriç, 2007). Many other methods of NO$_3^-$ removal have been explored such as reverse osmosis, ion exchange, ammonia stripping, electrodialysis, catalytic reduction, and electrocatalytic reduction (Kapoor and Viraraghavan, 1997; Yang and Lee, 2005; Della Rocca and Belgiorno V Meriç, 2007). Among these techniques, the electrocatalytic reduction of NO$_3^-$ is a promising and clean technology because the electron reductants neither introduce pollutants nor adversely affect the environment (Garcia-Segura et al., 2018; Gayen et al., 2018).

The mechanism of the electrochemical NO$_3^-$ reduction reaction (NO$_3^−$-RR) involves anodic oxidation and cathodic reduction in which NO$_3^-$ is reduced to NO$_2^-$, NH$_4^+$, and N$_2$ on the active sites of the cathode according to Eqs 1–3 (Zhang et al., 2021):

\[
\begin{align*}
\text{NO}_3^- + 2e^- + H_2O &\rightarrow \text{NO}_2^- + 2OH^- \quad \text{(1)} \\
\text{NO}_3^- + 6e^- + 6H_2O &\rightarrow \text{NH}_4^+ + 8OH^- \quad \text{(2)} \\
2\text{NO}_3^- + 10e^- + 6H_2O &\rightarrow N_2 + 12OH^- \quad \text{(3)}
\end{align*}
\]

The choice of the cathode material is important in this process. To date, most studies have used high-cost noble metal cathodes, such as Pt, Rh, and Pd, which may limit their commercial application (Taguchi and Feliu, 2007; Yang et al., 2014; Soto-Hernández et al., 2019). Co$_3$O$_4$ is a cost-effective catalyst, and the preparation of a CuO-Co$_3$O$_4$/Ti electrode by the sol-gel method for electrochemical reduction of NO$_3^-$ was recently reported (Yang et al., 2020). The system demonstrated the complete removal of NO$_3^-$ after 3 h at a current density of 20 mA/cm$^2$.

NO$_2^-$ and NH$_4^+$ generated at the cathode (Eqs. (1) and (2)) diffuse to the anode where they are adsorbed onto the surface and subsequently oxidized to NO$_3^-$ and N$_2$ (Eqs. (4) and (5)) (Zhang et al., 2021):

\[
\begin{align*}
\text{NO}_3^- + H_2O &\rightarrow \text{NO}_2^- + 2e^- + 2H^+ \quad \text{(4)} \\
2\text{NH}_4^+ &\rightarrow N_2 + 6e^- + 6H^+ \quad \text{(5)}
\end{align*}
\]

When Cl$^-$ is present in the electrolyte, the following reactions also occur at the anode (Eqs. 6–9) (Zhang et al., 2021):

\[
\begin{align*}
2\text{Cl}^- &\rightarrow Cl_2 + 2e^- \quad \text{(6)} \\
\text{Cl}_2 + H_2O &\rightarrow HOCl + Cl^- + H^+ \quad \text{(7)} \\
\text{HOCl} &\rightarrow ClO^- + H^+ \quad \text{(8)} \\
2\text{NH}_4^+ + 3\text{ClO}^- &\rightarrow N_2 + 3\text{H}_2O + 2H^+ + 3\text{Cl}^- \quad \text{(9)}
\end{align*}
\]

The electrochemical NO$_3^−$-RR involves NO$_3^-$ reduction at the cathode and ammonium nitrogen (NH$_4^+$-N) oxidation at the anode. Cl$_2$ generated at the anode (Eq. (6)) immediately forms hypochlorite (Eq. (7)), which selectively oxidizes NH$_4^+$ to N$_2$ (Su et al., 2017). Hence, the efficient anodic oxidation of chloride ions is a key requirement for this process, and the anode materials used in the chlor-alkali industry, which obtain Cl$_2$ by electrolysis of sodium chloride, provide a useful reference (Yi et al., 2007). Among these materials, IrO$_2$-RuO$_2$ is a good choice due to its low overpotential, high chlorine selectivity, and long-term stability (Chen et al., 2007). In addition, the electrocatalytic reduction of NO$_3^-$-N is also affected by reaction potential, current, solution pH, battery structure, and anode material.

Here, a catalytic cathode was prepared by the in situ electrodeposition of Co$_3$O$_4$ on a titanium substrate (Co$_3$O$_4$/Ti) to obtain improved electrocatalytic performance. IrO$_2$-RuO$_2$/Ti was employed as the anode for the effective removal of NH$_4^+$-N and TN. The aim of this study was to obtain simultaneous electrochemical NO$_3^-$ reduction and oxidation of the in situ-generated NO$_2^-$ and NH$_4^+$ into N$_2$ gas. The morphology and structure of Co$_3$O$_4$/Ti were characterized using conventional methods, and its performance in NO$_3^-$ removal was evaluated under different operating conditions. The current efficiency (CE) and energy consumption (EC) of the system were also measured to assess its commercial application.

### 2 Experimental Section

#### 2.1 Chemicals and Materials

The Ti mesh and Ti plate (99.5% purity, 0.6 mm, 10 mesh) were purchased from Lanruiyinde Electrochemical Materials Co., Ltd. (China). The Pt plate was obtained from Aidahengsheng Co., Ltd. (Tianjin, China). All chemicals were of analytical grade. Potassium nitrate and sodium hydroxide were purchased from Macklin Chemical Technology Co., Ltd. (Shanghai, China). Cobalt nitrate hexahydrate, sodium eosyl, hexachloroic acid, and ruthenium (III) chloride were obtained from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Solutions were prepared using deionized water (>15 MΩ cm) obtained from an Elix$^*$ 3 purification system (Millipore, United States). Simulated wastewater was prepared by adding potassium nitrate to deionized water.

#### 2.2 Preparation of Co$_3$O$_4$/Ti Cathode and IrO$_2$-RuO$_2$/Ti Anode

Samples of the Ti mesh and Ti plate (3 × 4 cm, 12 cm$^2$) were degreased with NaOH solution (40 wt%) at 95°C for 2 h before etching by boiling in oxalic acid solution (10 wt%) for 2 h. The treated samples were then rinsed with deionized water and stored in ethanol until further use.

As shown in Figure 1, the Co$_3$O$_4$/Ti electrode was prepared using an electrodeposition method. A three-electrode system was employed in a single compartment cell using the pretreated Ti mesh as the cathode, the Pt plate as the anode, and an Ag/AgCl...
reference electrode. The electrodeposition solution comprised boric acid (0.5 M), cobalt nitrate hexahydrate (0.1 M), and sodium eicosyl sulfonate (2.0 g/L). Following electrodeposition at a current of 0.25 A for 5 min, the electrode was washed with deionized water and oven-dried (60°C) before heating at 5°C/min to 500°C (hold 2 h) in a muffle furnace to effect calcination. The treated samples were allowed to cool naturally to room temperature.

The IrO2-RuO2/Ti anode was prepared by using a thermal decomposition method. A mixed solution of hexachloroiridic acid and ruthenium (III) chloride in n-butanol (molar ratio, 2:1) was evenly coated onto the surfaces of the pretreated titanium plate, dried at 105°C for 10 min, and then calcined at 500°C for 15 min. The process was repeated until the weight of the titanium plate increased by about 10 g/cm2. Finally, the electrode was washed with deionized water before use.

2.3 Characterization of the Co3O4/Ti Cathode

Surface morphology and elemental composition were studied by field-emission scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) on a Phenom ProX system (Thermo Fisher Scientific, United States) at an accelerating voltage of 15 kV. The crystal structure of Co3O4 was examined by X-ray diffraction (XRD) with an Xpert Powder system (Malvern Panalytical, Malvern, UK) using Cu Kα (λ = 1.5406 Å) irradiation.

2.4 Electrochemical Measurements

NO3−-RR tests were performed in a single chamber electrolytic cell (200 ml) using a three-electrode system, with Co3O4/Ti (or Ti as required), Pt plate, and Ag/AgCl as the working, counter, and reference electrodes, respectively. The electrolyte was prepared using Na2SO4 (0.1 M) and different concentrations of NO3−-N (KNO3) as required. Linear sweep voltammetry (LSV), and electrolysis tests were performed in an electrochemical workstation (Metrohm Autolab M204, Switzerland). Prior to the electrochemical test, oxygen was removed by bubbling high-purity N2 through the electrolyte for ≥20 min, and continuously fed during the experiments.

Electrolysis measurements were performed at an optimum current density of 15 mA/cm2, and aliquots of the reaction solutions (2 ml) were removed at predetermined time intervals to measure the concentrations of NO3−-N, NO2−-N, and NH4+-N. The effects of chlorine on NO3−-RR and the stability of the Co3O4/Ti cathode electrode were assessed at a current density of 15 mA/cm2 for 2 h and an initial NO3−-N concentration of 100 mg/L.

2.5 Analytical Methods

During the NO3−-RR, the formation of NO, N2O, and NH3 are negligible, and hence, the generated gaseous products can be considered as N2 (Teng et al., 2018). UV-Vis spectroscopy was used to measure the concentrations of NO3−-N, NO2−-N, NH4+-N, and total nitrogen (TN) (Evolution 201, Thermofisher Scientific Co., Ltd.), and their removal efficiencies were calculated according to Eqs (10)–(12):

\[
NO_3^- - N \text{ removal} = \frac{C_0(NO_3^- - N) - C_t(NO_3^- - N)}{C_0(NO_3^- - N)} \times 100% \tag{10}
\]

\[
NH_4^+ - N \text{ generation} = \frac{C_0(NH_4^+ - N) - C_t(NH_4^+ - N)}{C_0(NH_4^+ - N)} \times 100% \tag{11}
\]

\[
\text{TN removal} = \frac{C_0(TN) - C_t(TN)}{C_0(TN)} \times 100% \tag{12}
\]

where \( C_0(NO_3^- - N) \) (mg/L) is the initial concentration of NO3−-N, \( C_t(NO_3^- - N) \) (mg/L) is the concentration of NO3−-N at time t, \( C_t(NH_4^+ - N) \) (mg/L) is the concentration of NH4+-N at time t, \( C_0(TN) \) (mg/L) is the initial concentration of TN, and \( C_t(TN) \) (mg/L) is the concentration of TN at time t.

EC was calculated using Eq. 13 (Zhang et al., 2016):

\[
EC = \frac{U_{IT}}{V} \left( \frac{C_0 - C_t}{M \times Q} \right) \times n \times 96485 \times 100% \tag{13}
\]

where \( U \) is the cell potential (V), \( I \) is the current (A), \( t \) is the reaction time (h), and \( V \) is the volume of reaction solution (L).

The CE for TN removal rates was obtained using Eq. 14:

\[
\text{CE(%) } = \frac{(C_0 - C_t) \times V}{M \times Q} \times n \times 96485 \times 100% \tag{14}
\]

where \( M \) is the molar mass of N (14 g/mol), \( Q \) is the amount of electricity passing through the electrode, and \( n \) is the number of electrons obtained from the complete reduction of NO3−-N (calculated according to the conversion of NO3− to N, \( n = 5 \)).

3 RESULTS AND DISCUSSION

3.1 Electrode Characterizations and Chemical Tests

SEM was used to depict the electrode surface morphology of Co3O4/Ti. Figure 2 shows that spherical particles (3–5 μm) of Co3O4 were observed on the surface of Co3O4/Ti at different magnifications, confirming its deposition on the Ti mesh. SEM-EDS elemental mapping of a surface region of the Co3O4/Ti cathode (Figure 3) gave a value of 26.26 atom% for Co, indicating that the element was successfully deposited on the titanium mesh.

Figure 4 shows the XRD patterns of the calcined Co3O4/Ti electrode and their comparison with the reference powder patterns of cubic phase Co3O4 (PDF#42-1467) and Ti (PDF#44-1294). The characteristic peaks observed at 2θ of 35.1°, 38.4°, 40.2°, 53.0°, 62.9°, 70.7°, 76.2°, and 77.4° correspond to (100), (002), (101), (102), (110), (103), (112), and (201) planes of Ti (PDF#44-1294), respectively (Figure 4A). Inspection of the enlarged pattern obtained from the Co3O4/Ti cathode (Figure 4B) showed that the main peaks of Co3O4 at 2θ = 31.3°, 36.9°, 44.8°, 59.4°, 65.2°, and 74.1° correspond to the (220), (311), (400), (511), (440), and (620) planes of Co3O4, respectively. These results were in good agreement with the standard cubic phase (PDF#42-1467).
LSV was used to evaluate the electrocatalytic performance of the catalysts toward NO$_3^-$-RR. **Figure 5A** shows the LSV curves obtained with Co$_3$O$_4$/Ti and Ti in the presence of NO$_3^-$-N. The onset potential for NO$_3^-$-RR using the Co$_3$O$_4$/Ti cathode (-0.7 V) was more positive than that using the Ti mesh (-1.0 V), indicating the improved performance with the composite catalyst. From -0.7 to -1.6 V, Co$_3$O$_4$/Ti gave a larger current response at all potentials due to its higher activity toward the NO$_3^-$-RR compared with the Ti mesh. **Figure 5B** shows the effects of increasing NO$_3^-$-N (0–500 mg/L) using Co$_3$O$_4$/Ti as the cathode. In the absence of NO$_3^-$-N, the onset potential (i.e., for the electrolysis of water to produce H$_2$) was -0.9 V. The addition of NO$_3^-$ produced a positive shift in the onset potential, and the corresponding current increased with increasing initial NO$_3^-$-N due to the enhanced reduction reaction activity.

**FIGURE 2 |** SEM image of Co$_3$O$_4$/Ti at different resolutions.

**FIGURE 3 |** EDS elemental analysis of the surface of Co$_3$O$_4$/Ti cathode.
3.2 Effects of Electrochemical Reaction Parameters on NO₃⁻-RR Using the Co₃O₄/Ti Cathode

3.2.1 Catalytic Activity of the Co₃O₄/Ti Cathode

To determine the effect of Co₃O₄ on NO₃⁻ RR activity, the NO₃⁻-N (100 mg/L) removal efficiencies of the Co₃O₄/Ti and Ti mesh cathodes were compared at a current density of 15 mA/cm² with a Pt plate as the anode (Figure 6). The results showed that the Co₃O₄/Ti cathode could achieve a NO₃⁻-N removal efficiency of ~98% in 2 h, compared with 6.4% using the Ti mesh, demonstrating the important role of Co₃O₄ in improving the performance of NO₃⁻-RR.

3.2.2 Effects of Current Density

Figure 7A,B show the rate of NO₃⁻-N removal using the Co₃O₄/Ti cathode and the corresponding fit of the experimental data to first-order kinetics. The increased removal efficiency with increasing current density over 5–15 mA/cm² could be attributed to enhanced electron transfer on the electrode surface of Co₃O₄/Ti, which increased the rate of NO₃⁻-RR. However, when the current density was increased from 15 to 20 mA/cm², the removal efficiency of NO₃⁻-N did not improve significantly. At higher current densities, the competing hydrogen evolution reaction consumes the extra charge, and the NO₃⁻-N removal efficiency decreases. Figure 7C shows that there was good correspondence between the reduction of NO₃⁻-N and the generation of NH₄⁺-N. The reduction products were NH₄⁺-N and N₂, while NO₂⁻-N was not detected (Figure 7D).

3.2.3 Effect of Initial NO₃⁻-N Concentration

The effects of initial NO₃⁻-N concentration on its removal efficiency using the Co₃O₄/Ti cathode and the generation of reduction products are shown in Figure 8. At initial NO₃⁻-N concentrations of <100 mg/L, the removal efficiency of the system was close to 100% at 2 h; and the corresponding reduction products were NH₄⁺-N (60%) and N₂. At an initial NO₃⁻-N concentration of 200 mg/L, the removal efficiency decreased to ~58%, while the NH₄⁺-N generation efficiency increased to ~79%. Under this condition, the higher
initial NO$_3^-$-N concentration suppressed the competing hydrogen evolution reaction, thus reducing its charge consumption at the electrode.

### 3.3 Effects of Cl$^-$

The main product of electrocatalytic NO$_3^-$ reduction is NH$_4^+$, which is also a contaminant requiring removal. However, in the presence of Cl$^-$, which is widely present in drinking water and industrial water, the active species participating in the oxidative transformation of NH$_4^+$-N to N$_2$ at the anode (Eqs 6–9) will increase TN removal. The IrO$_2$-RuO$_2$/Ti electrode is widely employed in the chlor-alkali industry because of its high chlorine evolution performance. To investigate the effects of Cl$^-$ on NH$_4^+$-N generation and NO$_3^-$-N removal, various concentrations of Cl$^-$ were presented to a Co$_3$O$_4$/Ti/IrO$_2$-RuO$_2$/Ti NO$_3^-$-N removal system (Table 1). As the concentration of Cl$^-$ increased from 0 to 2000 mg/L, the removal efficiencies of NO$_3^-$-N were all >90%. At 4,000 mg/L Cl$^-$, the removal efficiency decreased to 83.99% due to the oxidation of NH$_4^+$ to NO$_3^-$ by HClO/ClO$^-$.

The increase in Cl$^-$ concentration increased the amount of HClO/ClO$^-$ generated by anodic oxidation to reduce NH$_4^+$-N to N$_2$. Hence, NH$_4^+$-N generation decreased and TN removal efficiency increased with increasing Cl$^-$ concentration. The TN removal efficiency reached 78.1% with negligible NH$_4^+$-N generation (0.34%) and without NO$_2^-$-N accumulation.

### 3.4 Long-Term Stability

In addition to the initial activity, the long-term performance of a catalyst is an essential requirement for its commercial application.
Figure 9 shows the changes in NO$_3^-$-N removal and distribution of generated products over 4 h, and 10 consecutive cycles of 2 h each, using the system. At an initial concentration of 100 mg/L, almost all NO$_3^-$-N is converted into N$_2$ after 4 h (Figure 9A). After 10 cycles (Figure 9B), the removal efficiencies of NO$_3^-$-N (~90%) and TN remained unchanged.

3.5 EC and CE
EC and CE are key evaluation factors for the commercial electrochemical treatment process (Zeng et al., 2020). The EC and CE under different process conditions using the system were calculated. It can be seen from Figure 10A,B that within 1 h after the start of the reaction, EC is lower and CE is higher than those of the follow-up experiments, but the NO$_3^-$-N removal rate is only 58.52%. After 2 h, the NO$_3^-$-N removal efficiency reaches 93.39% with an EC of 0.10 kW h/g NO$_3^-$-N and a CE of 40.3%. There was no significant improvement in the follow-up, but the EC continued to rise, and the CE continued to decline.

The effect of the initial NO$_3^-$-N concentration is demonstrated in Figures 10C,D. As the NO$_3^-$-N concentration increased, the EC decreased and CE increased. This can be explained by the increase in the contact area between NO$_3^-$-N and the electrode surface with increasing concentrations, which promotes the reduction reaction. From an economic viewpoint, the results indicate that the Co$_3$O$_4$/Ti IrO$_2$-RuO$_2$/Ti electrocatalytic process is more suitable for wastewater with high concentrations of NO$_3^-$-N. The small amount of NO$_3^-$ remaining in the electrochemically treated wastewater can be removed by other processes, such as the electrocatalytic removal of NO$_3^-$-N, which can be combined with constructed wetlands for wastewater control/remediation.

TABLE 1 | Effects of Cl$^-$ on the Co$_3$O$_4$/Ti IrO$_2$-RuO$_2$/Ti NO$_3^-$-N removal system.

| Cl$^-$ Concentration (mg/L) | NO$_3^-$-N removal (%) | NO$_2^-$-N generation (%) | NH$_4^+$-N generation (%) | TN removal (%) |
|---------------------------|------------------------|---------------------------|--------------------------|----------------|
| 0                         | 92.2                   | —                         | 54.5                     | 24.8           |
| 1000                      | 90.7                   | —                         | 37.2                     | 38.3           |
| 2000                      | 91.1                   | —                         | 19.9                     | 60.3           |
| 4,000                     | 84.0                   | —                         | 0.340                    | 78.1           |
4 CONCLUSION

A Co$_3$O$_4$/Ti electrode was successfully prepared by electrodeposition, and the material showed good electrocatalytic performance toward NO$_3^-$-RR. At an initial concentration of 100 mg/L NO$_3^-$-N, the removal rate was ~98% in 2 h (Pt anode; pH, 7.0; current density, 15 mA/cm$^2$). The corresponding generation of NH$_4^+$-N was ~60%, while NO$_2^-$-N was not detected. When IrO$_2$-RuO$_2$/Ti was employed as the anode in the presence of Cl$^-$ (2000 mg/L), the removal efficiencies for NO$_3^-$-N and TN under the same operating conditions were ~91% and ~60%, respectively, with an EC of 0.10 kW h/g NO$_3^-$-N and a CE of 40.3%. After 4 h of continuous operation, 100% of NO$_3^-$-N was converted into N$_2$. In addition, the system could maintain the removal
efficiencies of ~90% and ~60% for NO$_3^-$-N and TN, respectively, after 10 consecutive cycles (2 h each). This work provides a simple preparation method of electrodeposited Co$_3$O$_4$/Ti with good catalytic performance and stability, which provides a new preparation strategy for the Co$_3$O$_4$ catalytic electrode.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

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**AUTHOR CONTRIBUTIONS**

CW: conceptualization, methodology, data analysis, and writing—original draft. ZC: data curation. HH: validation. HL: resources and funding acquisition. SW: conceptualization, investigation, and writing—review and editing.

**FUNDING**

This work was supported by the National Natural Science Foundation of China (grant numbers 51978181, 51808527, 51727812, and 52131003).

**CONFLICT OF INTEREST**

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