

## Preparation of Co/Ti electrode by electro-deposition for aqueous nitrate reduction

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### ABSTRACT

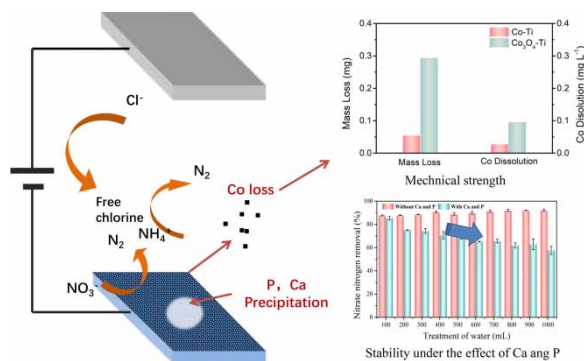
A Co/Ti electrode for nitrate reduction was prepared by electrode-deposition. In the single-compartment electrolysis cell, nitrate (100 mg/L) removal reached nearly 100% after 3 h electrolysis under the current density of 20 mA cm<sup>-2</sup> by using the Co/Ti electrode as cathode, and the main reduction products were ammonium nitrogen (66.5%) and nitrogen gas (33.5%). This performance on nitrate removal was comparable to a Co<sub>3</sub>O<sub>4</sub>/Ti electrode, and the electroactivity of the Co/Ti electrode towards nitrite reduction was higher than that of a Co<sub>3</sub>O<sub>4</sub>/Ti electrode. The Co/Ti electrode exhibited an improved stability with 18.7% of mass loss and 25.5% of Co dissolution compared with the Co<sub>3</sub>O<sub>4</sub>/Ti electrode after ultrasonic interference. The presence of chlorine ion (1,000 mg/L) could promote the total nitrogen (TN) removal to approximately 100% after 3 h electrolysis because of the ammonium oxidation by the free chlorine produced from the anode. In the presence of calcium (50 mg/L) and phosphate (0.5 mg/L), the nitrate removal decreased from 85.4 ± 1.5 to 57.7 ± 3.5% after ten reuse cycles. This result suggests that Ca and P should be pre-removed before the electro-reduction of nitrate.

**Key words:** Co/Ti, electrodeposition, electro-reduction, nitrate, stability

### HIGHLIGHTS

- Co/Ti electrode was prepared by electrode-deposition with nitrate removal of nearly 100%.
- The Co loss was improved comparing with the electrode prepared by thermal decomposition.
- The higher electroactivity towards nitrite reduction led to no nitrite detected.
- Ca and P decreased the nitrate removal for its precipitation onto the electrode.

### GRAPHICAL ABSTRACT



### INTRODUCTION

Excess nitrate in water has caused a serious problem due to its threats to both human health and ecological safety. Nitrate can produce nitrite and nitrosamines that pose direct harm to proteins or cells, causing diseases such as gastrointestinal cancers

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(Powlson *et al.* 2008). Moreover, it is considered as one of the important factors leading to lake eutrophication and red tide (McIsaac *et al.* 2001). Therefore, it is vital to remove nitrate from both drinking water and wastewater. China has limited the maximum level of  $15 \text{ mg L}^{-1}$  for total nitrogen for wastewater discharge which was issued in 2002 (NEPA 2002; Ye *et al.* 2019). The World Health Organization and many countries including the United States have set the limited maximum contaminant level of  $10 \text{ mg L}^{-1}$  for nitrate-nitrogen or  $50 \text{ mg L}^{-1}$  for nitrate in drinking water (NHCPRC 2006; USEPA 2010; WHO 2010).

Biological methods such as denitrification have been widely employed in wastewater plants, but the removal performance is negatively influenced by the limited carbon source and temperature (Molognoni *et al.* 2017; Zheng *et al.* 2021). Many physicochemical methods such as ion exchange, electro dialysis and chemical reduction have been developed. However, the concentrate waste produced from ion exchange, reverse osmosis, electro dialysis or the chemical release from chemical reduction led to secondary pollution and cost increases (Song *et al.* 2020; Hurtado-Martinez *et al.* 2021). Electrolysis for nitrate removal is recently causing attention due to its high removal efficiency, no chemical addition, simple operation and, in theory, no secondary pollution (Chen 2004). In an electrolysis cell, aqueous nitrate is reduced to nitrite ( $\text{NO}_2^-$ ) and subsequently to nitrous oxides ( $\text{NO}$ ,  $\text{N}_2\text{O}$ ), nitrogen gas ( $\text{N}_2$ ) and/or ammonia ( $\text{NH}_3$ ) on the cathode. The produced ammonia could be directly oxidized by anode or indirectly oxidized by free chlorine to  $\text{N}_2$ , which was generated by the anodic oxidation of the co-existing chloride. Up to now, many electrodes were developed for nitrate reduction by considering  $\text{N}_2$  selectivity, as reviewed by Garcia-Segura *et al.* (2018) and Zhang *et al.* (2021). The composite cathode of metal/metal oxides coated plate substrate(s), such as  $\text{Co}_3\text{O}_4/\text{Ti}$ ,  $\text{Fe}/\text{Cu}$ ,  $\text{Fe}/\text{C}$ ,  $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ ,  $\text{Pd-Cu}/\text{NiAl-LMO}$ , are generally better than a single-metal cathode for nitrate reduction (Su *et al.* 2017; Zhang *et al.* 2018; Gao *et al.* 2019; Bai *et al.* 2020). More specifically, Zhang *et al.* (2018) reported that the  $\text{Fe}/\text{Cu}$  electro-reduction system could remove 98.6% of  $\text{NO}_3^-$ -N within 90 min. In contrast, the removal of  $\text{NO}_3^-$ -N by a  $\text{Cu}$  or  $\text{Fe}$  electro-reduction system only reached up to 24.3 and 76.0%, respectively. Similarly, Gao *et al.* (2019) compared a  $\text{TiO}_2/\text{Ti}$  cathode with a  $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$  cathode for  $\text{NO}_3^-$ -N removal efficiency and found that the  $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$  cathode had a higher  $\text{NO}_3^-$ -N removal rate (80%) than that of the  $\text{TiO}_2/\text{Ti}$  cathode (45%).

Most of the previous studies did not focus on the life span of the electrode, which is an important factor for industrial application. In fact, the particles attached on the electrode surface are theoretically susceptible to fall off in the electrolyte solution during long-term work, which will reduce the performance for electrode reduction. It is reported that the electrode prepared by thermal decomposition showed a typical cracked mud-like structure, but its damage or life span has not been evaluated (Tian *et al.* 2007; Cheng *et al.* 2013). Electrodeposition possesses some advantages over the hydrothermal method, including low processing temperature, mildness of reaction, environmental friendliness, as well as low cost. Meanwhile, by simply changing the electrolyte composition and process adjustments, electrodeposition could obtain an optimized surface nanostructure and morphology, and better stability and reproducibility (Cai *et al.* 2019; Li *et al.* 2021). Thus, electrodeposition has received more attention. Moreover, natural water or wastewater contains complex inorganic/organic ingredients such as typical  $\text{Ca}$ ,  $\text{Mg}$ ,  $\text{C}$ ,  $\text{P}$ , and organic matters, which could limit the nitrate reduction. The ions of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  could precipitate near/at the electrode surface during the electrochemical removal of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  or  $\text{P}$  removal and recovery (Zeppenfeld 2011; Lei *et al.* 2017). However, there are few studies about the effect of these factors on nitrate electro-reduction.

The aim of this work was to prepare a cathode by the electroplating method for improving the stability to remove aqueous nitrate. A  $\text{Ti}$  plate was used as substrate due to its excellent performance for nitrate reduction with  $\text{Co}_3\text{O}_4$  attachment (Su *et al.* 2017; Yang *et al.* 2020). The prepared  $\text{Co}/\text{Ti}$  electrode was evaluated on its damage performance and nitrate removal behavior comparing with the  $\text{Co}_3\text{O}_4/\text{Ti}$  fabricated by thermal decomposition, and the possible nitrate reduction mechanism of the  $\text{Co}/\text{Ti}$  electrode was proposed. The effect of  $\text{pH}$  on  $\text{NO}_3^-$ -N and total nitrogen (TN) removal was studied. Meanwhile, we explored the effect of  $\text{Cl}^-$  on TN and further clarified the mechanism. In addition, the effect of the coexistence of  $\text{Ca}$  and  $\text{P}$  on nitrate reduction were also investigated.

## MATERIALS AND METHODS

### Materials and reagents

The  $\text{Ru-IrO}_2/\text{Ti}$  anode was purchased from Baoji Hengrui Titanium Anode Products Co., Ltd (Shanxi, China). The substrate for the cathode was titanium plate, which was purchased from Dongguan Huitai Alloy Material Co., Ltd (Guangdong, China). Cobalt chloride hexahydrate, sulfamic acid ( $\geq 99.5\%$ ), citric acid monohydrate ( $\geq 99.5\%$ ), and sodium dodecyl sulfate (SDS)

were purchased from Shanghai Macklin Biochemical Technology Co., Ltd (Shanghai, China). Saccharin sodium and basic potassium persulfate ( $\geq 99\%$ ) were obtained from Shanghai Yuanye Bio-technology (Shanghai, China) and Sigma-Aldrich (Shanghai, China), respectively. 1, 4-butyne diol ( $\geq 98\%$ ), sodium sulfate, sodium chloride, phosphoric acid were purchased from Nanjing Chemical Reagent (Jiangsu, China). Hydrochloric acid, sulfuric acid, potassium nitrate, sodium hydroxide, acetone, ethanol, boric acid, and potassium sodium tartrate tetrahydrate were all obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All reagents without purity noting were analytical grade without further purification during the experiment.

### Electrode preparation

Titanium substrate was polished with sandpaper and then etched in boiled sulfuric acid (20%) for 2 h. After washing by acetone, ethanol and deionized water in sequence, the substrate was dried in a 45 °C oven for 5 h. The substrate was used as cathode for electroplating with an Ru-IrO<sub>2</sub>/Ti anode in an electrolysis cell without chamber separating, which was filled with 100 mL of electrolyte solution containing cobalt chloride hexahydrate (2.75 g/L), boric acid (20.0 g/L), citric acid monohydrate (10.0 g/L), and one of sodium dodecyl sulfate (SDS, 0.15 g/L), saccharin sodium (0.20 g/L) or 1, 4-butyne diol (0.50 g/L). The distance between anode and cathode was 2.0 cm, and the current density was 30 mA cm<sup>-2</sup> provided by an auto range DC power supply (IT6922A, ITECH Electronic (USA) Co., Ltd) for 2 h of electroplating. The obtained cathode was washed with 300 mL of deionized water eight times and then naturally dried for characterization or application. The nitrate removal and test of the prepared cathode were compared with the Co<sub>3</sub>O<sub>4</sub>/Ti cathode, which was prepared by thermal decomposition as reported (Su *et al.* 2017).

### Characterization and test

A scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) patterns and electrochemical workstation were all employed for one of the prepared cathodes. For linear sweep voltammetry (LSV) tests, the prepared electrode was used as the working electrode. The Ru-IrO<sub>2</sub>/Ti electrode was used in electrolysis and a saturated calomel electrode (SCE) was used as a counter and reference electrode, respectively. The scan rate was 20 mV s<sup>-1</sup>, and the scan range was -1.2–0 V. The instruments were the same and the operation parameter was similar to that in our previous work with the scan rate of 20 mV s<sup>-1</sup> between -1.2 and 0 V (Yang *et al.* 2020). For the mechanical stability test of different cathodes prepared under different conditions, ultrasonic interference was carried out in a CNC ultrasonic cleaner (KH-300DE, Kunshan-Hechuang Co. Ltd (JiangSu, China)) at 100 KHz. After 15 min the electrodes of ultrasonic interference were all dried at 45 °C for 5 h, and then the weight loss was calculated.

### Nitrate removal

Nitrate reduction was conducted in an electrolysis cell without chamber separating at 25 °C, and the distance between anode (50 × 22 × 1 mm) and cathode (50 × 22 × 1 mm, l × w × t) was 2.0 cm. One hundred mL of solution with NO<sub>3</sub><sup>-</sup>-N (100 ppm) and Na<sub>2</sub>SO<sub>4</sub> (0.05 M) were added into the electrolysis cell, and the electrodes were all submerged into the solution. The current density was controlled at 20 mA cm<sup>-2</sup> for the electrolysis process with magnetic stirring at 600 rpm. Different cathodes prepared from different conditions were all used in nitrate removal. After that, the effect of inorganic matters was investigated by using a 45 × 20 × 1 mm cathode. For the effect of Cl<sup>-</sup>, NaCl at different amounts was added into the electrolysis solution with different concentrations of NO<sub>3</sub><sup>-</sup>-N and Na<sub>2</sub>SO<sub>4</sub> (0.05 M).

For the effect of Ca, different amounts of CaSO<sub>4</sub>·2H<sub>2</sub>O were added in the electrolysis solution with 100 mg/L NO<sub>3</sub><sup>-</sup>-N, 0.05 M Na<sub>2</sub>SO<sub>4</sub> and 100 mg/L NaHCO<sub>3</sub> as the inorganic carbon. For the effect of co-existence of Ca, P and Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O were added in the electrolysis solution containing Ca<sup>2+</sup> (50 mg/L), NO<sub>3</sub><sup>-</sup>-N (100 mg/L) and Na<sub>2</sub>SO<sub>4</sub> (0.05 M). During the electrolysis, the solution was sampled for the measurement of nitrate, ammonia, nitrite, and total nitrogen (TN). For the stability evaluation, the optimized Co/Ti and Co<sub>3</sub>O<sub>4</sub>/Ti electrodes were used for ten batch tests. The 100 mL aqueous nitrate solution at the initial concentration of 100 mg/L was added in the electrolysis cell for a subsequent batch after 3 h of electrolysis. In addition, the nitrate solution containing Ca<sup>2+</sup> (50 mg/L) and P (0.5 mg/L) was also used for these ten batch tests.

### Analytical methods

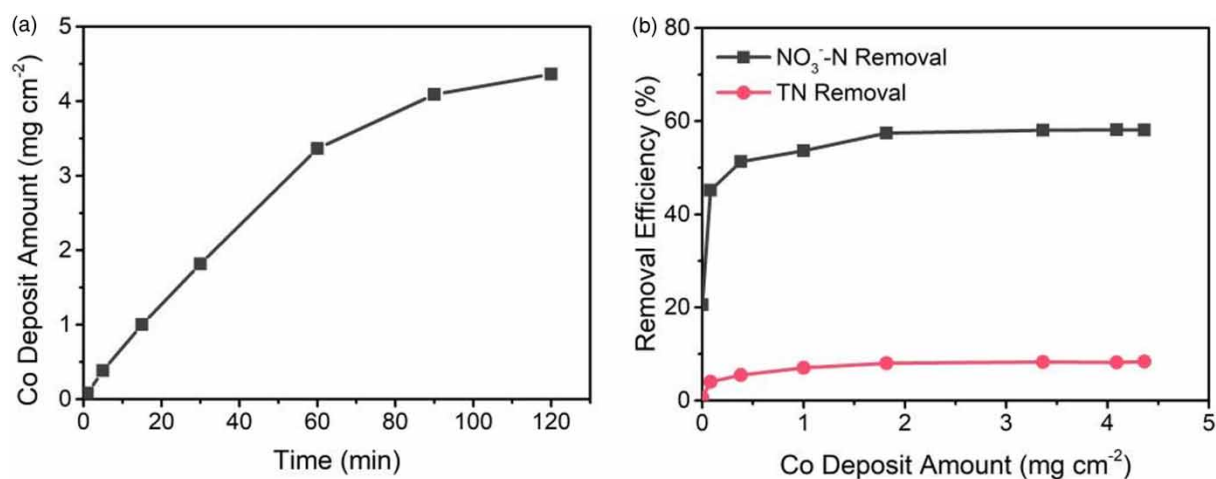
The analysis of nitrate, nitrite, ammonia and total nitrogen are described in the previous work (Yang *et al.* 2020). Briefly, the ion chromatography method was applied for nitrate and nitrite measurement. Nessler's reagent spectrophotometry method and alkaline potassium persulfate digestion UV spectrophotometric method were used respectively for the determination of

the concentration of ammonia and TN. In this work, the concentration of  $\text{Co}^{2+}$  and  $\text{Ca}^{2+}$  was measured by using an inductively coupled plasma-atomic emission spectrometer (iCAP-7400, Thermo Fisher, USA).

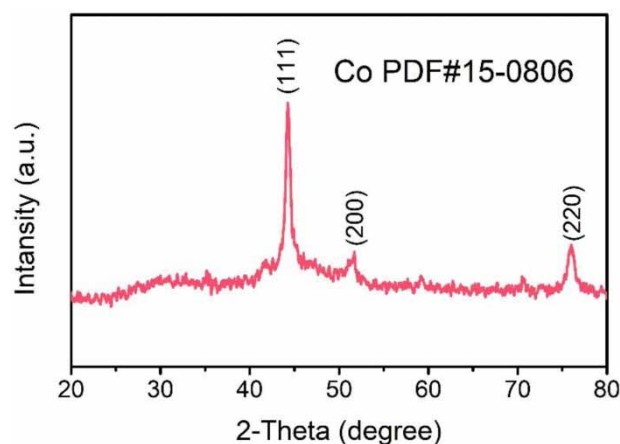
## RESULTS AND DISCUSSION

### Electrode preparation and characterization

The electro-deposition kinetic of Co on Ti substrate is shown in Figure 1(a). It was found that the amount of the electrode weight increased sharply in the initial 60 min, and the weight increase gradually slowed down to  $4.36 \text{ mg cm}^{-2}$  at 120 min. Different electrodes with Co amounts from 0 to  $4.36 \text{ mg cm}^{-2}$  were used for nitrate electro-reduction over 1 h. The nitrate removal increased dramatically from 20.6 to 45.2% with the Co electro-deposition amount from 0 to  $0.8 \text{ mg cm}^{-2}$ , which reached the maximum value of 58.1% when the Co electro-deposition amount was higher than  $1.81 \text{ mg cm}^{-2}$ . It was also found that the removal of TN increased from 0.6 to 8.3%, which could be explained by the direct oxidation of the increased ammonium on anode (Figure 1(b)). XRD was used for the electrode characterization, and the result indicated that Co crystals were generated on the surface of Ti substrate (Figure 2). Therefore, the electrodeposition process can be described as follows:



**Figure 1** | (a) The relationship between different electrodeposition time and the amount of Co electrodeposition; and (b) the removal efficiencies of  $\text{NO}_3^-$ -N and TN in 60 min for electrodes with different Co electrodeposition amounts.

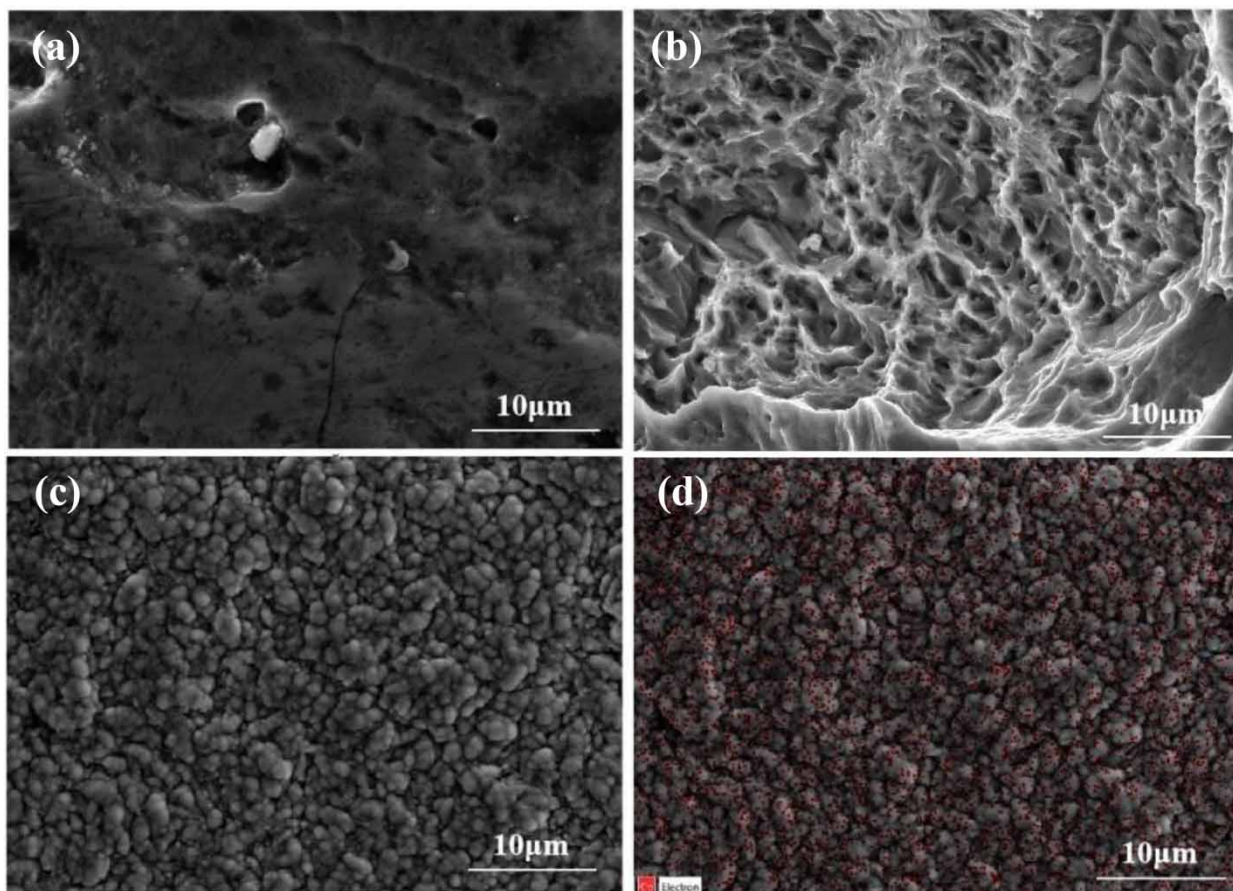


**Figure 2** | The XRD patterns of Co/Ti electrode.

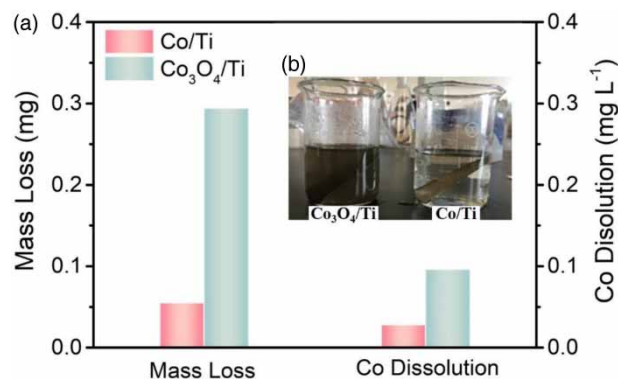
Figure 3 shows the surface morphology of Ti substrate,  $\text{Co}_3\text{O}_4/\text{Ti}$  and  $\text{Co}/\text{Ti}$  electrodes, respectively. A rough surface attached with a large number and dense particles in appearance can be observed after electro-deposition, and the EDS images indicated that the 1–3  $\mu\text{m}$  Co particles were uniformly distributed on the surface of Ti substrate. This surface morphology was different from the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode with a cracked mud-like surface structure, which was prepared by thermal decomposition. This result was similar to that reported by previous literature (Tian *et al.* 2007; Cheng *et al.* 2013), and the picture taken also shows a clear difference between the three electrodes (Supplementary Material, Figure S1).

In our electro-deposition process, the typical additives for surface improvement, such as SDS, saccharin sodium and 1,4-butynediol, respectively, at different concentrations, were employed to improve mechanical stability. To test the mechanical stability of the electrode, ultrasonic interference was applied on the electrode emerging in distilled water at 100 kHz. The result indicated that the mass loss of the electrode significantly increased as the concentration of saccharin sodium or 1,4-butynediol increased, while the SDS concentration increase improved the mass loss of the electrode with the mass loss from 0.21 mg decreasing to 0.055 mg. The effect of the three additives on Co dissolution was not obviously observed. Moreover, the addition of SDS or saccharin sodium had little effect on nitrate removal, while the nitrate removal decreased by nearly 10% as the 1,4-butynediol concentration increased to  $0.5 \text{ g L}^{-1}$  in the electrode preparation process.

The  $\text{Co}/\text{Ti}$  electrode prepared by electro-deposition and the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode prepared by the typical thermal decomposition method were also used for ultrasonic interference treatment in order to compare their stability. As shown in Figure 4, the water immersed by the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode turned black, but the water immersed by the  $\text{Co}/\text{Ti}$  electrode showed little change in color, indicating that some materials on the electrode surface fell off. Specifically, the surface structure of the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode is easily affected by human operation and high temperature extreme environments, resulting in uneven surface distribution and different thickness. Thus, the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode could easily fall off. In contrast, the electrodeposition method used the electroplating solution to prepare the  $\text{Co}/\text{Ti}$  electrode, and the material on the  $\text{Co}/\text{Ti}$  electrode



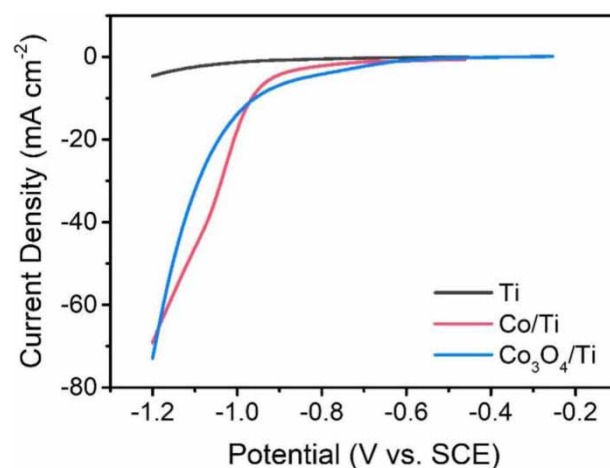
**Figure 3** | SEM image of Ti substrate (a),  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode (b) and  $\text{Co}/\text{Ti}$  electrode (c). EDS images of the  $\text{Co}/\text{Ti}$  electrode (d).



**Figure 4** | The mass loss and the Co dissolution of the Co/Ti and Co<sub>3</sub>O<sub>4</sub>/Ti electrodes (a) and photo of the two electrodes in water after ultrasonic test (b). (100 mL, 100 mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>-N, 0.05 M Na<sub>2</sub>SO<sub>4</sub>, 20 mA cm<sup>-2</sup>, 180 min).

surface was tightly attached, making it more difficult to fall off. In addition, the mass loss and Co dissolution were further measured to clarify the phenomenon. Compared with the 0.294 mg of mass loss and 0.094 mg of dissolution for the Co<sub>3</sub>O<sub>4</sub>/Ti electrode, the Co/Ti electrode exhibited an excellent mechanical stability with 0.055 mg of mass loss and 0.024 mg of dissolution (Figure 4(a)). Meanwhile, the SEM images of the Co/Ti electrode before and after ultrasonic interference treatment were also measured (Supplementary Material, Figure S2). After the ultrasonic interference treatment, no significant effect on the electrode surface morphology was observed, and only a small part of the material attached to the Co/Ti electrode surface fell off, indicating excellent mechanical stability. Notably, although the mass loss of the electrode causes the secondary pollution of the treated water, both the electrodes after the mass loss showed no decrease in nitrate removal (Supplementary Material, Figure S3). This result is consistent with the observation from Figure 1(b), which suggests that the maximal removal obtained at a low Co electro-deposition amount (1.81 mg cm<sup>-2</sup>). The Co electro-deposition amount we used was 4.41 mg cm<sup>-2</sup>, which means that the loss of 0.055 and 0.024 mg had no effect on its removal performance.

The LSV test provides electroactivity of the electrodes for oxidation and reduction. In our previous work, Ti substrate and a Co<sub>3</sub>O<sub>4</sub>/Ti electrode were compared in the absence or presence of 100 mg/L nitrate with Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte. Relevant literature demonstrated the current increase over the potential range of -0.7 to -1.0 V for a Ti based electrode were mainly attributed to NO<sub>3</sub><sup>-</sup> reduction to NO<sub>2</sub><sup>-</sup>, and the current increase over the potential range of -0.9 to -1.2 V was mainly caused by the NO<sub>3</sub><sup>-</sup> converted to NH<sub>3</sub> or the NO<sub>2</sub><sup>-</sup> reduction (Wang *et al.* 2017; Yang *et al.* 2020). The process of nitrate reduction to nitrite was generally the rate-limiting step for nitrate removal (Montesinos *et al.* 2015; Yang *et al.* 2020). Figure 5 provides the LSV results of Ti substrate, and Co/Ti and Co<sub>3</sub>O<sub>4</sub>/Ti electrodes towards nitrate reduction. It

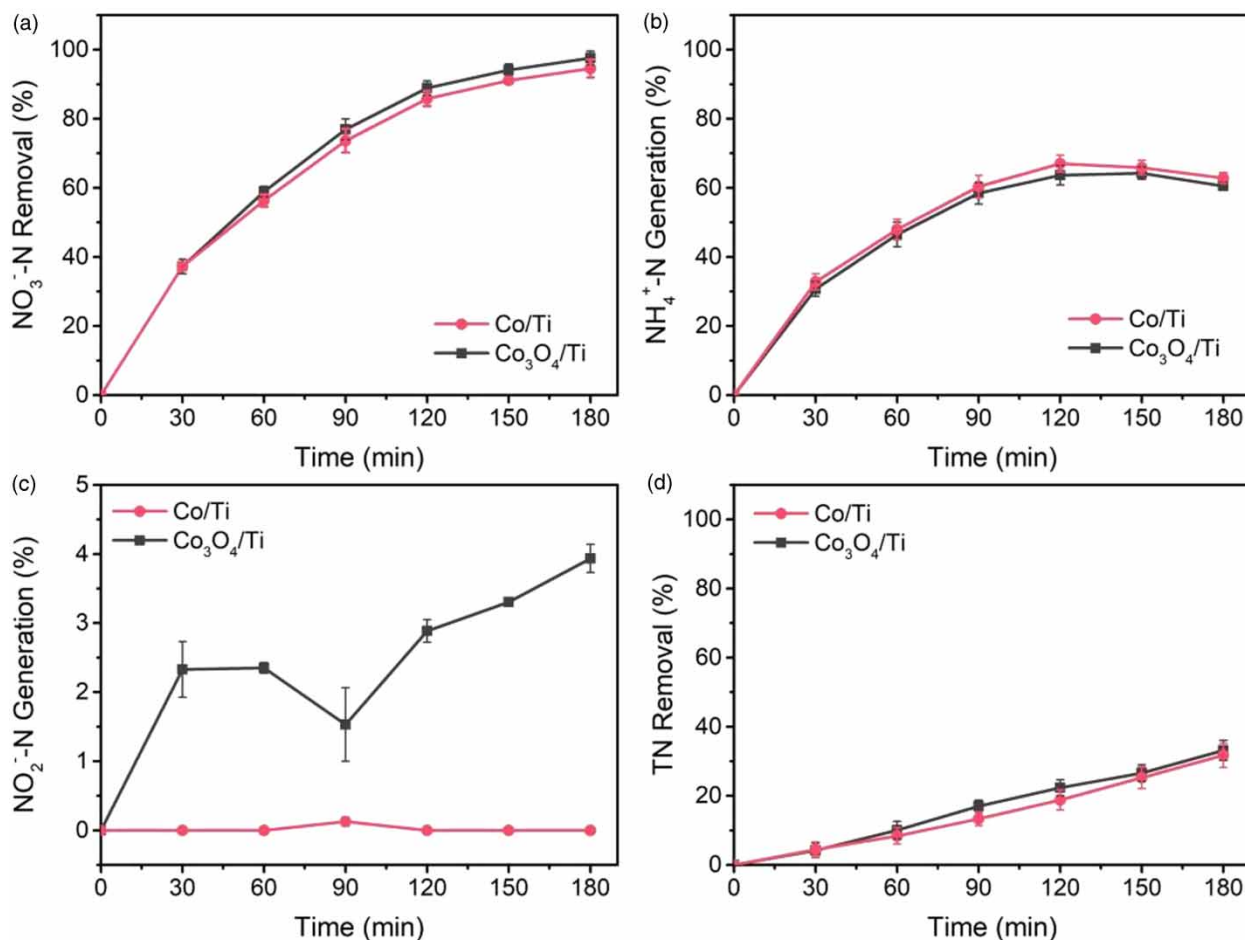


**Figure 5** | Linear sweep voltammetry (LSV) of Ti, Co/Ti and Co<sub>3</sub>O<sub>4</sub>/Ti electrodes in 100 mL 100 mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>-N with 0.05 M Na<sub>2</sub>SO<sub>4</sub> solution, scan rate: 20 mV s<sup>-1</sup>.

can be seen that the current density was much larger for the Co/Ti and  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode than that for Ti substrate over the potential increase from  $-0.7$  to  $-1.2$  V, indicating better electroactivity for both Co/Ti and  $\text{Co}_3\text{O}_4/\text{Ti}$  electrodes than Ti substrate. The difference could be ascribed to surface morphology improvement, thereby modifying the electronic structure and enhancing electron transfer (Wang *et al.* 2017). Obviously, compared with LSV of the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode, the smaller values of current density of the Co/Ti electrode over the range of  $-0.7$  to  $-1.0$  V, and the larger values of current density of the Co/Ti electrode over the range of  $-1.0$  to  $1.18$  V were observed. The result suggests that the Co/Ti electrode had better electroactivity towards  $\text{NO}_3^-$  conversion to  $\text{NH}_3$  and  $\text{NO}_2^-$  reduction and a weaker electroactivity towards  $\text{NO}_3^-$  reduction to  $\text{NO}_2^-$ . This result on the improved electroactivity on nitrite reduction could decrease the nitrite generation, as confirmed in the results in Figure 6(c). It is also noted that the potential of hydrogen evolution overlapped the potential range ( $-1.0$  to  $-1.2$  V), which implied a possibility that there is a higher electroactivity of hydrogen evolution for the Co/Ti electrode than the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode.

### Nitrate reduction

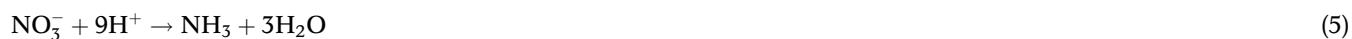
To evaluate the nitrate reduction performance of the prepared electrode the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode, which has excellent treatment ability, was used for comparison. The concentration of  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N,  $\text{NO}_2^-$ -N and TN during the 3 h electrolysis is shown in Figure 6. The Co/Ti electrode exhibited a comparable kinetic performance on  $\text{NO}_3^-$ -N reduction with 97% of nitrate removal, 62% of  $\text{NH}_4^+$ -N generation and 37% of TN removal.  $\text{NO}_2^-$ -N generation was not observed for the Co/Ti electrodes, while 4% of nitrogen was reduced to  $\text{NO}_2^-$ -N for the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode, which is consistent with the LSV result of the better electroactivity on nitrite reduction. A small decrease of  $\text{NH}_4^+$ -N generation after 2 h could be explained by anode oxidation



**Figure 6** | (a)  $\text{NO}_3^-$ -N removal, (b)  $\text{NH}_4^+$ -N generation, (c)  $\text{NO}_2^-$ -N generation and (d) TN removal obtained by Co/Ti and  $\text{Co}_3\text{O}_4/\text{Ti}$  electrodes (100 mL,  $100 \text{ mg L}^{-1}$   $\text{NO}_3^-$ -N,  $0.05 \text{ M Na}_2\text{SO}_4$ ,  $20 \text{ mA cm}^{-2}$ , 180 min).

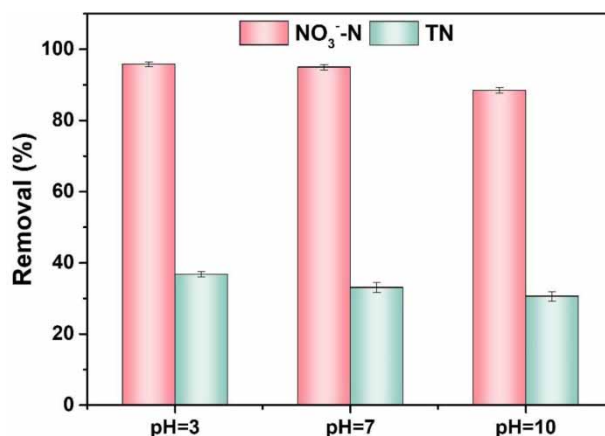
and  $\text{NH}_3$  volatilization, as was discussed in previous work (Yang *et al.* 2020). Thirty-seven per cent of TN removal means that 36% of  $\text{NO}_3^-$ -N may be eventually removed from solution as  $\text{N}_2$  or  $\text{NH}_3$  gas. Considering the maximum generation of  $\text{NH}_4^+$ -N (66.5%), it can be seen that the main products of Co/Ti cathode reduction were  $\text{NH}_4^+$ -N (66.5%  $\text{NO}_3^-$ -N) and nitrogen-containing gas ( $\text{N}_2$  or  $\text{NH}_3$ , 33.5%  $\text{NO}_3^-$ -N), of which the  $\text{NO}_3^-$ -N transfer portion was coincidentally consistent with the reaction as described in previous work (Yang *et al.* 2020). It means that the Co/Ti cathode had no selectivity towards  $\text{N}_2$  or  $\text{NH}_4^+$ -N. In addition, these results on  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N and TN change for the Co/Ti cathode are all comparable to that of the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode. However, there was no  $\text{NO}_2^-$  detected in the system of the Co/Ti cathode, which could be explained by the better electroactivity towards nitrite reduction of the Co/Ti cathode than the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode.

Based on the above results, the possible nitrate reduction mechanism of the Co/Ti electrode was proposed. Under the electrochemical treatment, the main conversion route of  $\text{NO}_3^-$  is usually reduced to  $\text{NO}_2^-$ ,  $\text{N}_2$ ,  $\text{NH}_3$  (Equations (3)–(5)), and the  $\text{NO}_2^-$  is further converted to  $\text{N}_2$  (Equation (6)) (Garcia-Segura *et al.* 2018). Notably, according to related research, high  $\text{Co}^{2+}$  content could generate more  $\text{SO}_4^{\bullet-}$ , which was beneficial to the production of  $\bullet\text{OH}$  (Equation (7)) (Zou *et al.* 2019; Zhu *et al.* 2020). Thus, it could improve the ammonia complete degradation (Equation (8)), compared with the Ti electrode. In addition, the  $\text{NO}_3^-$  could be reduced to  $\text{NO}_2^-$  by the effect of  $\text{Co}^0$  (Equation (9)), and then the  $\text{NO}_2^-$  was further converted to  $\text{N}_2$  or  $\text{NH}_4^+$  (Equations (10) and (11)) (Tang *et al.* 2019). The formation of a large number of  $\text{NH}_4^+$  also hinders further denitrification:



### Effect of pH on $\text{NO}_3^-$ -N and TN removal

In the electrochemical treatment process, pH also plays an important role in the removal of contaminants (Zou *et al.* 2019; Zhu *et al.* 2020). The effect of pH on  $\text{NO}_3^-$ -N and TN removal was explored in our experiment, and the result indicated that a slight decrease as the pH increased from 3 to 10 (Figure 7). The result was different from that reported by Yao *et al.* (2021),



**Figure 7** | Variation in  $\text{NO}_3^-$ -N and TN removal at different initial pH values (pH = 3, 7 and 10).



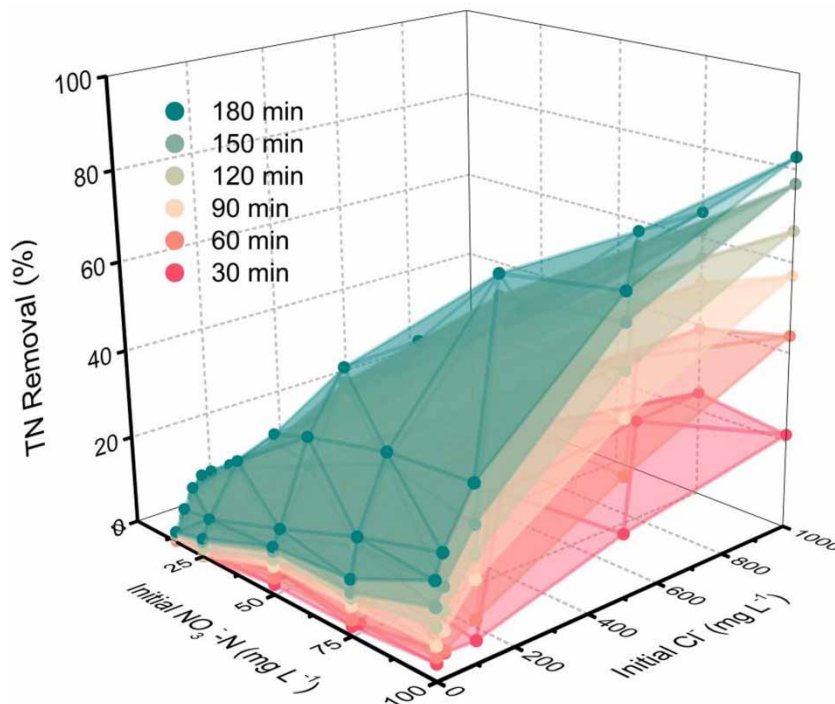
who found that the  $\text{NO}_3^-$ -N removal was the lowest at pH 7, which was nearly 50% lower than that of pH 3 by using the Ti electrode as cathode. However, Tang *et al.* (2019) found that pH 9 was best for nitrate reduction as the function of  $\text{Fe}^0$ ,  $\text{Cu}^0$  and the chelating resin by the Fe-Cu/D407 cathode. Therefore, the different effect of pH value may be attributed to the different electrode materials used.

### Effect of $\text{Cl}^-$ ion

The effect of  $\text{Cl}^-$  on TN removal was well understood as a result of  $\text{NH}_4^+$ -N oxidation to  $\text{N}_2$  by the free chlorine generated from anode oxidation of  $\text{Cl}^-$ , which was the main mechanism of TN removal for electro-reduction of nitrate in most studies (Garcia-Segura *et al.* 2018; Zhang *et al.* 2021). Figure 8 shows a 3D graph of TN removal, and thus the TN removal could be simply estimated as the function of initial concentration of  $\text{NO}_3^-$  and  $\text{Cl}^-$ . It can be seen that the TN removal increased from 20.9% to the maximum value of 82.6% as the initial concentration of the co-existing  $\text{Cl}^-$  increased from 0 to 1,000 mg/L at the initial  $\text{NO}_3^-$  concentration of 100 mg/L. It is noted that the  $\text{NO}_3^-$ -N removal was approximately 83.0% under the initial  $\text{Cl}^-$  concentration of 1,000 mg/L after 3 h-electrolysis, indicating that the selectivity of  $\text{NO}_3^-$ -N reduction for TN removal was nearly 100%. As is known, the addition of  $\text{Cl}^-$  has a certain removal effect on total nitrogen. The increase in the removal of TN by  $\text{Cl}^-$  was mainly due to the decrease in the content of ammonia nitrogen. According to Equations (12)–(14) (Ye *et al.* 2020),  $\text{ClO}^-$  produced by oxidation of  $\text{Cl}^-$  could oxidize ammonia nitrogen into nitrogen for denitrification:



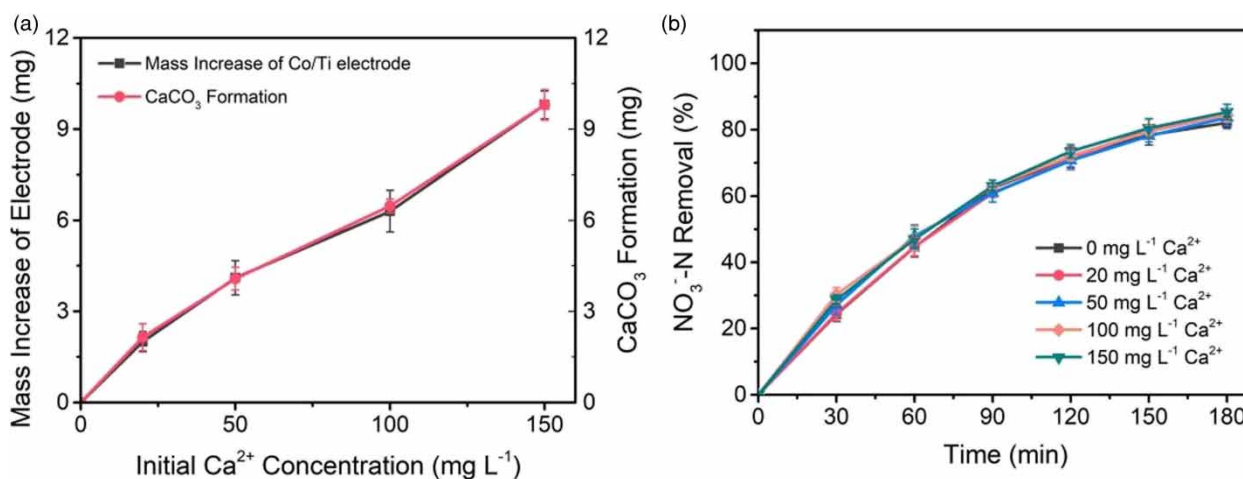
At the same time, the presence of  $\text{Cl}^-$  will inhibit the reduction of nitrate, thereby decreasing the efficiency of reducing  $\text{NO}_3^-$  to nitrogen. In the process of ammonia oxidation under the effect of  $\text{ClO}^-$ , ammonia nitrogen will also produce  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N, resulting in a decrease in the denitrification efficiency. Therefore, the addition of  $\text{Cl}^-$  has no synergistic effect on the removal of nitrate. Notably, compared with Figure 6(a), (100%), the addition of  $\text{Cl}^-$  reduced the removal of nitrate (83%) by 18.2%.



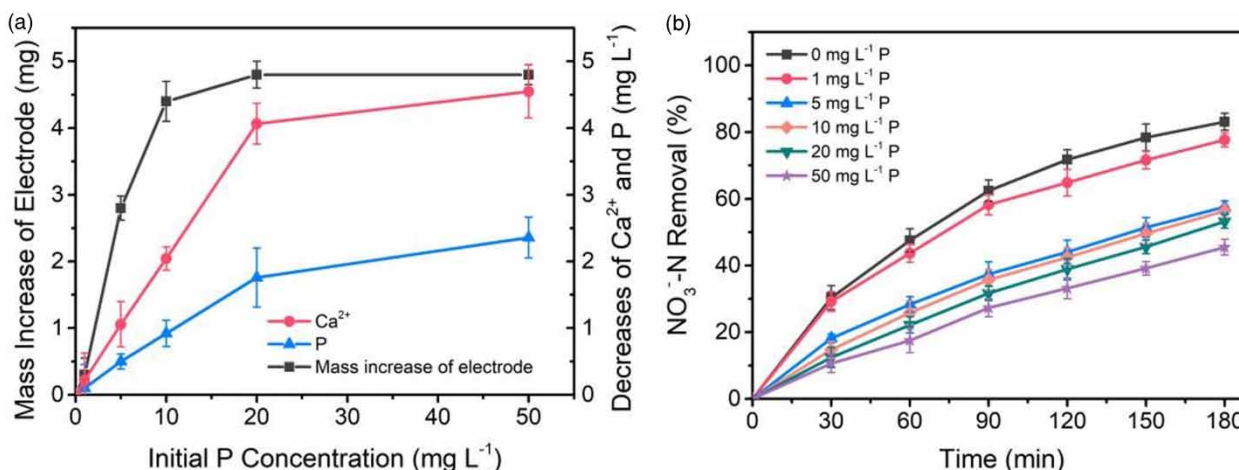
**Figure 8** | TN removal for the Co/Ti electrode under the effect of  $\text{NO}_3^-$ -N concentration and  $\text{Cl}^-$  concentration in different reaction times (100 mL, 0.05 M  $\text{Na}_2\text{SO}_4$ , 20 mA  $\text{cm}^{-2}$ , 180 min). Please refer to the online version of this paper to see this figure in color: <http://dx.doi.org/10.2166/wrd.2021.047>.

### Effect of coexistence $\text{Ca}^{2+}$ ion

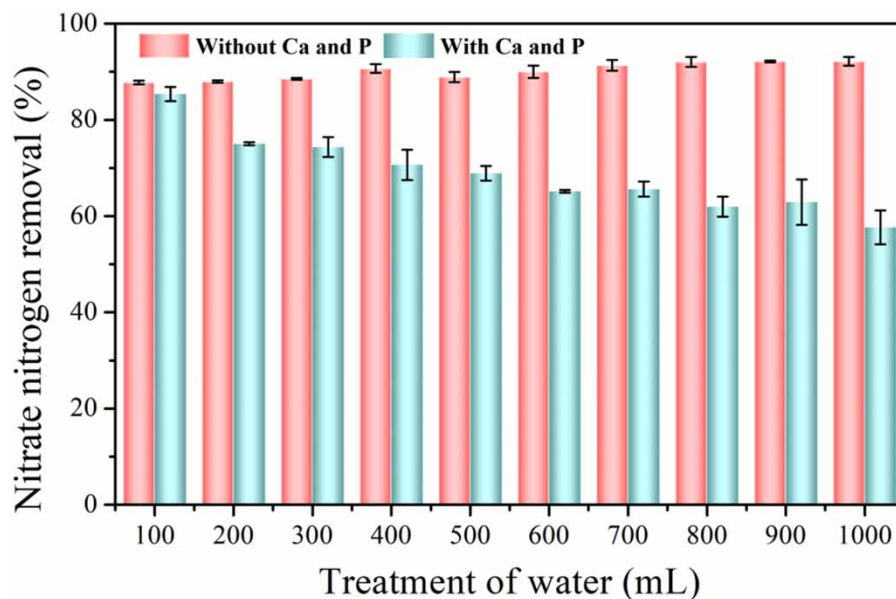
The effect of co-existing Ca on nitrate removal was investigated in this work. Figure 9 shows the effect of  $\text{Ca}^{2+}$  in the presence of  $\text{NaHCO}_3$  as inorganic carbon of 100 mg/L. It was found that the increased weight of electrode was 9.8 mg at the initial  $\text{Ca}^{2+}$  concentration of 150 mg/L, which is equal to the formation of  $\text{CaCO}_3$  precipitation as calculated by the decreased  $\text{Ca}^{2+}$  concentration in solution (Figure 9(a)). The white crystal-like matter on the cathode surface center could be observed, and the result of XRD pattern confirmed the white crystal-like matter is  $\text{CaCO}_3$  (Supplementary Material, Figure S4). This phenomenon indicated that the  $\text{HCO}_3^-$  converted to  $\text{CO}_3^{2-}$  as the result of pH increase and generated  $\text{CaCO}_3$  on the surface of the cathode. All the precipitation formed on the cathode surface rather than solution suggested that this precipitation process in solution was limited by the  $\text{OH}^-$  diffusion. However, this precipitation effect on the performance of nitrate reduction was not observed. Figure 10 shows the effect of P on nitrate removal in the presence of  $\text{Ca}^{2+}$  at 50 mg/L. As the P concentration increased from 0 to 50 mg/L, the nitrate removal greatly decreased from 83.1 to 45.5%. It was found that the weight of electrode increased by 4.8 mg when the initial P concentration was increased to 20 mg/L and the concentration of  $\text{Ca}^{2+}$  and P was decreased. The ratio of the decreased amount of  $\text{Ca}^{2+}$  and P was nearly 2:1, suggesting the precipitation was  $\text{Ca}_3(\text{PO}_4)_2$ . This result indicated that the coexistence of Ca and P have a greater adverse effect on nitrate removal.



**Figure 9** | (a) Mass increase of Co/Ti electrode and  $\text{CaCO}_3$  formed in solution, (b)  $\text{NO}_3^-$ -N removal for Co/Ti electrode at different concentrations of initial  $\text{Ca}^{2+}$  (100 mL, 100 mg L<sup>-1</sup>  $\text{NO}_3^-$ -N, 0.05 M  $\text{Na}_2\text{SO}_4$ , 20 mA cm<sup>-2</sup>, 180 min). Please refer to the online version of this paper to see this figure in color: <http://dx.doi.10.2166/wrd.2021.047>.



**Figure 10** | (a) Mass increase of Co/Ti electrode and the decrease of  $\text{Ca}^{2+}$  and P in solution, (b)  $\text{NO}_3^-$ -N removal for Co/Ti electrode at different concentrations of initial P and 50 mg L<sup>-1</sup>  $\text{Ca}^{2+}$  (100 mL, 100 mg L<sup>-1</sup>  $\text{NO}_3^-$ -N, 0.05 M  $\text{Na}_2\text{SO}_4$ , 20 mA cm<sup>-2</sup>, 180 min). Please refer to the online version of this paper to see this figure in color: <http://dx.doi.10.2166/wrd.2021.047>.



**Figure 11** | The removal of  $\text{NO}_3\text{-N}$  after ten cycles (100 mL/cycle) for Co/Ti electrode ( $100 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$ ,  $0.05 \text{ M Na}_2\text{SO}_4$ ,  $20 \text{ mA cm}^{-2}$ , 180 min). Please refer to the online version of this paper to see this figure in color: <http://dx.doi.10.2166/wrd.2021.047>.

### Stability performance

The stability or electrode working life is an important index for the industrial application. We replaced nitrate solution with fresh solution after 3 h of electrolysis nine times, and the removal performance is shown in Figure 11. It was found that the Co/Ti electrode exhibited excellent stability on nitrate removal of  $90.0 \pm 2.2\%$  without a significant decrease after ten reuse cycles. In the presence of Ca (50 mg/L) and P (0.5 mg/L), the nitrate removal of the Co/Ti electrode significantly decreased from  $85.4 \pm 1.5$  to  $57.7 \pm 3.5\%$ , indicating the presence of Ca (50 mg/L) and P (0.5 mg/L) has a significant adverse effect on Co/Ti electrode. A possible explanation could be that the generation of hydroxide ions around the surface of the cathode promotes the formation of the Ca, P precipitation on the electrode surface.

### CONCLUSIONS

A Co/Ti electrode was prepared by electrodeposition and characterized by XRD and SEM. The removal of nitrate and the effect of coexisting  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$  and  $\text{HPO}_4^{2-}$  ions on nitrate removal by using the Co/Ti electrode as cathode were all investigated. Comparing to a  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode prepared by the typical thermal decomposition method, the Co/Ti electrode exhibited an excellent mechanical stability with 18.7% of mass loss and 25.5% of Co dissolution of  $\text{Co}_3\text{O}_4/\text{Ti}$  electrode after ultrasonic interference. Aqueous nitrate was reduced to ammonium nitrogen (66.5%) and nitrogen gas (33.5%) with nearly 100% of nitrate removal. Nitrite was not detected during the electrolysis process because of its high electroactivity towards nitrite reduction. The presence of chlorine ion (1,000 mg/L) could convert all the nitrate (100 mg/L) to nitrogen gas after 3 h of electrolysis. The presence of calcium ion (150 mg/L) has little effect on nitrate removal regardless of  $\text{CaCO}_3$  precipitation on the surface of the electrode in our experiment short-term test, while the coexistence of calcium ion and hydrogen phosphate ion have a greater adverse effect on nitrate removal, with a 49% reduction. Although the Co/Ti electrode exhibited excellent stability on nitrate removal without a significant decrease after ten reuse cycles, the presence of Ca (50 mg/L) and P (0.5 mg/L) decreased the removal from  $85.4 \pm 1.5$  to  $57.7 \pm 3.5\%$ . This result suggests that Ca and P should be pre-removed before the electrolysis process.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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