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PII: S0045-6535(22)00299-5
DOI: https://doi.org/10.1016/j.chemosphere.2022.133806
Reference: CHEM 133806

To appear in: ECSN

Received Date: 12 November 2021
Revised Date: 11 January 2022
Accepted Date: 28 January 2022

Please cite this article as: Hong, X., Du, Y., Zhang, H., Xue, W., San Hui, K., Fang, G., Electrochemical nitrate removal by magnetically immobilized nZVI anode on ammonia-oxidizing plate of RuO$_2$–IrO$_2$/Ti, Chemosphere (2022), doi: https://doi.org/10.1016/j.chemosphere.2022.133806.

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Author contributions statement

Xiaoting Hong, Yingying Du, Haibin Zhang, Wenjuan Xue contributed to the conception of the study;

Yingying Du, Wenjuan Xue performed the experiment;

Xiaoting Hong, Yingying Du contributed significantly to analysis and manuscript preparation;

Xiaoting Hong, Yingying Du performed the data analyses and wrote the manuscript;

Kwan San Hui, Gangming Fang helped perform the analysis with constructive discussions;

Xiaoting Hong, Yingying Du, and Haibin Zhang contributed to the revision of the manuscript.
Graphical abstract
Electrochemical nitrate removal by magnetically immobilized nZVI anode on
ammonia-oxidizing plate of RuO$_2$-IrO$_2$/Ti

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Abstract

Ammonium as the major reduction intermediate has always been the limitation of nitrate reduction by cathodic reduction or nano zero-valent iron (nZVI). In this work, we report the electrochemical nitrate removal by magnetically immobilized nZVI anode on RuO₂-IrO₂/Ti plate with ammonia-oxidizing function. This system shows maximum nitrate removal efficiency of 94.6 % and nitrogen selectivity up to 72.8 % at pH of 3.0, and it has also high nitrate removal efficiency (90.2 %) and nitrogen selectivity (70.6 %) near neutral medium (pH=6). As the increase of the applied anodic potentials, both nitrate removal efficiency (from 27.2 % to 94.6 %) and nitrogen selectivity (70.4 % to 72.8 %) increase. The incorporation of RuO₂-IrO₂/Ti plate with ammonia-oxidizing function on the nZVI anode enhances the nitrate reduction. The dosage of nZVI on RuO₂-IrO₂/Ti plate (from 0.2 g to 0.6 g) has a slight effect (the variance is no more than 10.0 %) on the removal performance. Cyclic voltammetry, Tafel analysis and electrochemical impedance spectroscopy (EIS) were further used to investigate the reaction mechanisms occurring on the nZVI surfaces in terms of CV curve area, corrosion voltage, corrosion current density and charge-transfer resistance. In conclusion, high nitrate removal performance of magnetically immobilized nZVI anode coupled with RuO₂-IrO₂/Ti plate may guide the design of improved electrochemical reduction by nZVI-based anode for practical nitrate remediation.

Keywords: nanoscale zero-valent iron (nZVI); electrochemical removal; N₂ selectivity; nitrate;
1. Introduction

Excessive application of nitrogen fertilizers and substantial discharge of treated or accidental leakage of untreated wastewater have led to an increase in nitrate concentrations in water bodies and become a common environmental problem (Zhang et al., 2018; Aggrwal et al., 2021; Ma et al., 2021). Nitrate is easily converted to nitrite by microorganisms in the human body, and nitrite can oxidize low-iron hemoglobin, which normally carries oxygen in the blood, to methemoglobin, thus losing its oxygen-carrying capacity and causing tissue hypoxia, making it difficult to breathe and causing acute poisoning and damage to the nervous system (Wei et al., 2018; Singh et al., 2022). In addition, nitrite reacts with secondary amines to form substances that are carcinogenic and teratogenic to humans (Yang et al., 2018). It is therefore becoming increasingly important to raise awareness of the existence of these health hazards issues indirectly caused by nitrates. The World Health Organization (WHO) has set a limit of 11.3 mg L\(^{-1}\) for NO\(_3\)-N in drinking water (Puggioni et al., 2021).

In recent years, environmental scientists have conducted numerous studies on the remediation technology of nitrate pollution. There are three main types of nitrate pollution remediation techniques including physicochemical remediation, bioremediation, and chemical reduction according to their principles (Fan et al., 2021; Liu et al., 2021; Pang and Wang, 2021). The physicochemical methods mainly include distillation, electrodialysis, reverse osmosis, ion exchange with high cost and ordinary efficiency. Biological remediation is the use of denitrifying bacteria to transform
nitrate into nitrogen, but this technique is generally limited to areas with good geological conditions and small contaminated areas. Chemical reduction remediation is a fast and effective remediation method that uses certain reducing agents to reduce the nitrate in the water (Ramalingam and Subramania, 2021). Zero-valent iron (ZVI) has attracted great attention for an excellent alternative (Liu and Wang, 2019). Especially, nano zero-valent iron (nZVI) has become one of the most widely used reducing agents due to its higher reactivity and better removal efficiency (Khalil et al., 2018).

Various researches have been conducted to optimize the reaction conditions (dosage, temperature, current densities, co-existing ions, etc.) (Guo et al., 2020), synergistic reaction with other reagents such as persulfate (Wang et al., 2021b), intermediate products (Zhang et al., 2017), nZVI based-composites (Jiang et al., 2012; Qi et al., 2021; Wu et al., 2021), and doped nZVI (Su et al., 2014), etc. for nitrate reduction. Among these reduction reactions the most difficulty is to steadily enhance the N$_2$ selectivity and elucidate the reaction mechanisms and pathways. Recently, one of the nitrate reduction research directions under external stimuli of an applied electrical field has gained strong interest. Most conventionally, electrocoagulation (EC) or a combination of EC and electrooxidation (EO) was studied as a denitrification process to efficiently remove nitrate by iron or aluminum plate anodes (Amarine et al., 2020; Benekos et al., 2021). Ti/RuO$_2$ anode was combined to enhance the N$_2$ selectivity and removal efficiency of iron EC system for the treatment of actual wastewater containing high concentration of nitrate ion based on the anodic ammonia
oxidation (Chauhan and Srivastava, 2020; Li et al., 2021; Pellessier et al., 2021).

Novel nZVI nanostructures were also explored to achieve high nitrate removal efficiency and N₂ selectivity by electrocatalytic denitrification (Wang et al., 2021a). All of the above-mentioned electrocatalytic researches were about cathodic nitrate reduction. However, nZVI related electrocatalytic denitrification via anodic nitrate reduction is rarely reported.

In this study, nZVI-related composite anodes constructed on RuO₂-IrO₂/Ti electrode (nZVI/ RuO₂-IrO₂/Ti) by magnetic force immobilization were used to explore the synergistic effects of intrinsic reduction property of nZVI, anodic current, ammoniation characteristic of RuO₂-IrO₂/Ti, and nZVI electro-coagulation on the nitrate removal. Electrochemical denitrification activity and N₂ selectivity was evaluated under different reaction parameters such as the combination of the composite anode, nZVI dosage, initial solution pH, background electrolyte, applied voltage, and initial nitrate concentration. The underlying reaction mechanisms of electrocatalytic denitrification were proposed. The final results showed that the experimental system is of great significance for denitrification treatment of water with high performance about nitrate removal efficiency and N₂ Selectivity.

2 Materials and methods

2.1 Materials and reagents

The pH of aqueous solution was adjusted by 3 M of NaOH or 1 M of H₂SO₄ in each experiment. The conductivity of aqueous solution was adjusted by 500 mg L⁻¹ of
Na₂SO₄. Furthermore, nZVI was purchased from Shanghai Xiangtian Nano Material Co., Ltd. RuO₂-IrO₂/Ti plate and graphite sheet were supplied by Suzhou Shude Industrial Machinery Co., Ltd. Nitrate solution was prepared with ultrapure water using NaNO₃.

2.2 Experimental setup

Electrochemical denitrification experiments were carried out in 500 mL glass jars. Different initial concentrations (50, 100 and 500 mg L⁻¹) of nitrate solution with a volume of 400 mL were prepared using sodium nitrate. Different concentrations of Na₂SO₄ (0, 250, 500 mg L⁻¹) were used as the background electrolyte. The area of RuO₂-IrO₂/Ti plate immersed in the solution was ~ 45 cm². A certain amount of nZVI powder was uniformly distributed on the RuO₂-IrO₂/Ti plate with a dimension of 16.5 × 3.0 cm². The nZVI powders were fixed to the RuO₂-IrO₂/Ti plate surface by a 2.8 cm × 7.8 cm × 0.4 cm magnet labeled as nZVI-RuO₂-IrO₂/Ti composite anode. An nZVI-graphite composite anode was also prepared using same method with a graphite plate. A pure graphite cathode was connected in parallel to the anode at a distance of 1.5 cm under different applied voltages. The experimental setup is shown in Fig. 1.

![Experimental setup diagram](image-url)
2.3 Experimental methods

Many factors affecting nitrate removal were investigated, including anode material, applied voltage, initial pH, nano-zero-valent iron dose, electrolyte concentration, initial nitrate concentration. The nZVI-RuO$_2$-IrO$_2$/Ti, mZVI-RuO$_2$-IrO$_2$/Ti, iron filings-RuO$_2$-IrO$_2$/Ti, RuO$_2$-IrO$_2$/Ti, and nZVI-graphite were used as the anodes in this study. The effects of various applied voltages of 1.2 V, 3.0 V, 5.0 V, 10.0 V and initial pH values of 3, 6, 10 on the nitrate removal were studied. Different electrolytes of FeSO$_4$, FeCl$_2$ and Na$_3$PO$_4$ (500 mg L$^{-1}$) were also used to explore their effects on nitrate removal compared to Na$_2$SO$_4$. Each experiment was conducted for 5 h with a sampling interval of 0.5 h and thereafter each sample was filtered through a membrane filter (pore size of 0.45 μm) before testing. The concentrations of nitrate, nitrite and ammonium were determined by ion chromatography (Eco-IC, Metrohm). Iron ions were analyzed spectrophotometrically by forming the reddish-orange tris complex of iron (II) and 1,10-phenanthroline. The pH and conductivity of the solution were measured by pH meter (FiveEasy, METTLER TOLEDO).

The percentage of nitrate removal ($R_{\text{NO}_3^-}$), N$_2$ selectivity ($S_{\text{N}_2}$) of the electrochemical denitrification were calculated using the following equations (Wang et al., 2021a):

$$R_{\text{NO}_3^-} = \frac{[\text{NO}_3^-]_0 - [\text{NO}_3^-]_t}{[\text{NO}_3^-]_0} \times 100\%$$

Eq. (1)
The subscripts of 0 and f in the equation represent the initial and final concentrations (mg L\(^{-1}\)) of NO\(_3^−\), NO\(_2^−\), and NH\(_4^+\), respectively. All samples were analyzed at least in triplicate.

2.4 Characterization techniques

The final precipitate of the reaction as well as the residual nZVI were collected, filtered, and then dried at 80°C under vacuum. X-ray powder diffraction (XRD) patterns of the resultant precipitate and nZVI (before and after reaction) were recorded using the DX-2700 (Dandong Haoyuan Instrument) diffractometer with monochromatic Cu Ka irradiation in the 20 angular regions between 10 ° and 80 °. The surface morphology, atomic composition and distribution of the precipitate were measured by scanning electron microscopy equipped with a dispersive X-ray spectroscopy detector (SEM/EDS, Inspect F50, FEI). Different valence states of Fe and oxygen in final precipitate were measured by X-ray photoelectron spectroscopy (XPS) (K-Alpha, Thermo Fisher Scientific). The split-peak fitting operations were performed by XPSPEAK41 software. Tafel analysis, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were used to strengthen the mechanism interpretation by an electrochemical workstation (Chenhua, CHI 660A, Shanghai). Tafel curves were measured at nitrate solution with an initial concentration of 100 mg L\(^{-1}\) and 0.6 g of nZVI. EIS diagram was carried out at an initial voltage of -0.3 V with high frequency of 10\(^5\) and low frequencies of 10\(^{-2}\). Cyclic voltammetry
curves were obtained at a scanning rate of 100 mV s\(^{-1}\) between -1.8 and 1.8 V (versus Ag/AgCl).

2. Results and discussion

3.1 Effect of different reaction parameters on electrochemical denitrification

3.1.1 Anode materials

The comparative NO\(_3^-\) reduction efficiency on different anodes such as nZVI-RuO\(_2\)-IrO\(_2\)/Ti, mZVI-RuO\(_2\)-IrO\(_2\)/Ti, iron filings-RuO\(_2\)-IrO\(_2\)/Ti, RuO\(_2\)-IrO\(_2\)/Ti and nZVI-graphite was depicted in Fig. 2a. Additionally, direct spreading nZVI into nitrate solution without electric field was also investigated to compare the denitrification result. Obviously, the nitrate removal efficiency on nZVI-RuO\(_2\)-IrO\(_2\)/Ti anode was significantly higher than that in single RuO\(_2\)-IrO\(_2\)/Ti or nZVI system. The NO\(_3^-\) concentration was finally reduced to 5.42 mg L\(^{-1}\) and the removal rate reached 94.6 % on nZVI-RuO\(_2\)-IrO\(_2\)/Ti anode after 5 h under the conditions of initial nitrate concentration of 100 mg L\(^{-1}\), voltage of 10V, temperature of 25 °C, pH of 3, electrolyte concentration of 500 mg L\(^{-1}\) Na\(_2\)SO\(_4\) and nZVI dosage of 0.6g. In contrast, the nitrate removal rates of RuO\(_2\)-IrO\(_2\)/Ti anode and nZVI alone under the same reaction conditions were only 18.3 % and 28.4 %, respectively. Either nZVI or RuO\(_2\)-IrO\(_2\)/Ti on nZVI-RuO\(_2\)-IrO\(_2\)/Ti was replaced by mZVI and iron fillings or graphite, the removal rate was decreased to 77.6 %, 78.9 %, and 82.4 %, respectively.
Fig. 2 Influence of different factors on nitrate removal, a) anode materials, b) electrolyte concentrations, c) initial pH, d) dose of nZVI, e) applied voltages, f) initial nitrate concentrations.

As indicated on Fig. 3a, the main intermediate of electrochemical nitrate reduction on these different electrodes is NH$_4^+$ and the toxic intermediate NO$_2^-$ was negligibly detected in all cases. The anode composition has a very important influence on the
intermediate and the $N_2$ selectivity. Correspondingly, nitrate reduction on nZVI-RuO$_2$-IrO$_2$/Ti electrode has a higher value of $N_2$ selectivity (72.8 %) than other electrodes (e.g., 63.8 % for nZVI-graphite electrode), which is comparable to previous result (74.0 %) conducted on ordered mesoporous carbon nZVI cathode elsewhere (Teng et al., 2018).

3.1.2 Electrolyte concentration

Fig. 2b shows the effect of different electrolyte concentrations on nitrate removal for nZVI-RuO$_2$-IrO$_2$/Ti electrode. Initially, the nitrate removal rate was 85.3 % without addition of Na$_2$SO$_4$. The gradual increase of the removal rate to 90.12% and 94.6 % was observed for the systems with 250 and 500 mg L$^{-1}$ Na$_2$SO$_4$, respectively. Similar trends were observed for the value of $N_2$ selectivity which increases from 68.3 % to 70.9 % and 72.8 % with the increase the electrolyte concentration from 0 mg L$^{-1}$ to 250 and 500 mg L$^{-1}$, respectively (Fig. 3b). Obviously, increasing the electrolyte concentration could not only enhance the nitrate removal rate, but also improve the $N_2$ selectivity. Higher concentration of supporting electrolyte leads to stronger anodic dissolution, thus protecting the nZVI particles from passivation (Katsounaros and Kyriacou, 2007).

Three different background electrolyte of FeSO$_4$, FeCl$_2$ and Na$_3$PO$_4$ with 500 mg L$^{-1}$ were used to investigate the effect of Fe$^{2+}$, Cl$^-$ and PO$_4^{3-}$ on the nitrate removal efficiency. Unexpectedly, substituting Na$_2$SO$_4$ with FeSO$_4$ dramatically reduced the nitrate removal efficiency from 94.6 % to 20.2 %. Although surface-bound Fe$^{2+}$ may
enhance the electron transfer from the nZVI core to the solid–liquid interface, and thus improve the performance of the nitrate reduction by nZVI (Huang and Zhang, 2005). However, nZVI was bound on the anodes in this study and positive charged Fe$^{2+}$ were hard to surface bound due to its preference to migrate to the cathode surface. Further replacing Na$_2$SO$_4$ with other iron electrolyte of FeCl$_2$, the nitrate removal efficiency was partially recovered to 84.8 %. The presence of chloride ions could significantly accelerate the reaction rate for NH$_4^+$ oxidation on supporting anode of RuO$_2$-IrO$_2$/Ti and subsequently the nitrate reduction reaction moves forward direction (Sun et al., 2020; Song et al., 2021). Apparently, the nitrate removal efficiency in Na$_3$PO$_4$ (93.2 %) was very close to that of Na$_2$SO$_4$ system (94.6 %).

### 3.1.3 Initial pH

The effect of various initial pH values (3.0, 6.0, and 11.0) of electrolyte on the electrocatalytic nitrate reduction of nZVI-RuO$_2$-IrO$_2$/Ti was performed under the same initial conductivity. A drop from pH 11.0 to 3.0 enhanced both the nitrate removal efficiency from 72.4 % to 94.6 % (Fig. 2c) and N$_2$ selectivity from 70.5 to 72.8 % (Fig. 3c). Nitrate reduction is a protons consumption process ($4\text{Fe}^0 + \text{NO}_3^- + 10\text{H}^+ \rightarrow 4\text{Fe}^{2+} + \text{NH}_4^+ + 3\text{H}_2\text{O}$ $\Delta G=-997.71$ (Alowitz and Scherer, 2002), $2\text{NO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2+ 6\text{H}_2\text{O}$ (Li et al., 2016)), thus acidic condition is more favorable for high nitrate removal rate and N$_2$ selectivity by coupling the protons and electrons. As each reaction proceeds, the slope of the removal rate tends to be more flat because the gradual increase of the background solution pH in all cases is detrimental to the nitrate reduction. The rapid decline in the nitrate removal rate is
attributed to a rapid passivation of the iron surface under alkaline conditions, while the acidic condition assists in dissolving the surface (hydr)oxide layer, and reveals more active sites for the electrochemical nitrate removal (Salam et al., 2015).

**Fig. 3** Concentrations of NO$_3^-$, NO$_2^-$ and NH$_4^+$ ions in solution with different a) anode materials, b) electrolyte concentrations, c) initial pH, d) dose of nZVI, e) applied voltages, and f) initial nitrate concentrations.
3.1.4 Dosage of nZVI

Fig. 2d shows the effect of the dosage of nZVI on nitrate removal. As previously mentioned, the nitrate removal efficiency was only 18.3 % when RuO₂-IrO₂/Ti was used as the anode without nZVI and significantly increased when nZVI coupling with RuO₂-IrO₂/Ti was used as the anode. As the amount of nZVI increased to 0.2 and 0.6 g, the removal efficiency dramatically increased to 86.0 % and 94.6 %. Correspondingly, the N₂ selectivity of nZVI/RuO₂-IrO₂/Ti with 0.2 g or 0.6 g nZVI is 71.0 % and 72.8 % (Fig. 3d). Obivously, the adding nZVI improves the nitrate removal efficiency and N₂ selectivity in a way that the higher the amount of nZVI, the higher the removal of nitrate and N₂ selectivity.

3.1.5 Applied voltage

As shown in Fig. 2e, applied voltage has a great influence on the removal of nitrate indicating that higher current densities lead to the faster nitrate removal. In half hour the nitrate residual (92 mg L⁻¹) is only slightly lower than the initial concentration of 100 mg L⁻¹ at applied voltage of 1.2 V. The values are gradual decrease to 83 and 80 mg L⁻¹ at applied voltage of 3.0 and 5.0 V. In the case of 10.0 V the residual nitrate rapidly fall to 55 mg L⁻¹. The final removal efficiency of nitrate at applied voltages of 1.2 V, 3.0 V, 5.0 V, and 10.0 V were 27.2 %, 49.6 %, 69.1 % and 94.6 % after 5 h, respectively. As the increase of applied voltage from 1.2 V to 10.0 V, the N₂ selectivity slightly increases from 70.4 % to 72.8 % (Fig. 3e).
3.1.6 Initial nitrate concentration

The nitrate removal performance were investigated with nitrate electrolyte of different concentrations of 50 mg L\(^{-1}\), 100 mg L\(^{-1}\) and 500 mg L\(^{-1}\), respectively (Fig. 2f). At the conditions of 10.0 V, pH=3, 500 mg L\(^{-1}\) Na\(_2\)SO\(_4\), 25\(^\circ\)C and 0.6g nZVI, the nitrate removal efficiencies were 95.6 %, 94.6 % and 3.0 % at initial concentrations of 50 mg L\(^{-1}\), 100 mg L\(^{-1}\) and 500 mg L\(^{-1}\) nitrate respectively. It was clear that the denitrification efficiency was very high for both the initial nitrate concentration of 50 mg L\(^{-1}\) and 100 mg L\(^{-1}\), but the nitrate removal efficiency fell to 3.0 % when the initial nitrate concentration was as high as 500 mg L\(^{-1}\). Studies have shown that high initial NO\(_3^-\) concentrations lower NO\(_3^-\) removal efficiencies because more ions are present in the treated water (Salam et al., 2015), therefore, more time is required for their removal (Salam et al., 2015). As can be seen from Fig. 3f, the N\(_2\) selectivity of systems with 50 mg L\(^{-1}\) and 100 mg L\(^{-1}\) nitrate (72.3 and 72.8 %) is also much larger than that of 500 mg L\(^{-1}\) nitrate (60.8 %).

3.2 The iron ions and pH variation with the reaction

In this study all electrochemical nitrate reduction reaction finally leads to a higher pH value for background solution. The most representative parameter of applied voltage variation (3.0 V, 5.0 V and 10.0 V) was selected to investigate its effect on background solution pH along with the contact time (Fig. S1a). The background solution pH was sharply increased from 3 to 10 in one hour under an applied voltage of 10.0 V, however, it took 2.0 and 2.5 h to reach ~ 10 (pH value) for
3.0 V and 5.0 V systems. Subsequently, all of the background solutions fluctuate near a pH of 10. Understandably, the background solution pH increase rate is positively correlated with the increase of the applied voltage. Both the nitrate reduction reaction and nZVI coagulation (or corrosion) process were very violent at high voltage.

Meanwhile, nitrate reduction reaction consumes more protons at higher voltage and stronger coagulation leads to more alkaline flocs in the solution. Therefore, a large amount of OH⁻ was rapidly produced in the solution resulting in high value pH.

Fig. S1b showed the production of ferrous iron and total iron ions in the solution during the nitrate reduction reaction. The concentration of ferrous iron ions rapidly reached 12.8 mg L⁻¹ in ten minutes due to violent anodic electro-dissolution, subsequently, the amount of ferrous iron ions fell sharply to an undetectable value in another fifteen minutes because of fast oxidation by dissolved oxygen from water electrolysis. Then, the presence of ferrous iron ions was no longer detectable in the solution in the rest of the reaction. The total iron content increased persistently in the first four hours of the reaction and decreased slightly in the last hour, probably due to the excessive consumption of nZVI corrosion or greatly enhanced coagulation process.

3.2 The characteristics of iron-related precipitate

The surface morphology and elemental composition of the precipitation were characterized using SEM with an EDS detector. SEM image revealed that the precipitates are of rough and irregular shapes with nanosized domain in an
agglomeration state (Fig. 4a). The elemental distributions and elemental compositions
of the precipitates were shown in Fig. 4b and Fig. 4c. The elemental mapping images
indicated that there are three elements (Fe, O and N) and these elements were evenly
distributed on the surface of the precipitates. EDS spectrum showed that the
composition of the precipitate contained 87.0 % Fe, 7.0 % O and 1.0 % N element,
respectively.

Fig. 4. a) SEM images, b) elemental mapping of precipitation, c) EDS spectrum of
precipitates, and XRD images of d) nZVI before reaction, e) nZVI after reaction and
precipitates.
XRD patterns of the precipitate, nZVI before and after reaction were displayed in Fig. 4d and Fig. 4e, respectively. The diffraction peaks at 20 angles of 44.67 ° and 64.9 ° accord with peaks of native nZVI (standard card PDF#99-0064) (Su et al., 2019). In addition to the characteristic peak of intrinsic nZVI at 20 of 44.67 °, the XRD pattern of nZVI after reaction also exhibits peaks at 20 of 30.07 °, 35.56 °, 43.12 °, 44.74 °, 53.65 °, 57. 34 ° and 62.74° that were assigned to the typical characteristics of iron oxides (Fe₃O₄, JCPDS 72-2303) and iron hydroxides (γ-FeOOH, JCPDS 74-1877) (Fig. 4b). The precipitation collected from the reaction solution also exhibited same peaks of iron oxides and iron hydroxides which indicates the fact that part of the precipitate was adhered to the nZVI surface during the reaction (Fig. 4b) (Huang et al., 2020).

XPS measurements were also performed to investigate the composition and the chemical state of the precipitate. Fig. 5a shows the XPS spectra of the precipitates revealing the presence of C, Fe, O, N and S in the sample. N and S elements were contributed by the nitrate/intermediates and sulphate electrolyte. The Fe 2p spectrum consisted of Fe 2p₃/₂ and Fe 2p₁/₂ peaks with two characteristic satellites with a Fe²⁺/Fe³⁺ ratio of 1.46:1. The high resolution Fe 2p₃/₂ deconvolution spectra show one peak at 711.34 eV for divalent iron and another peak at 713.05 eV for trivalent iron (Bae and Lee, 2014; Chen et al., 2018), which confirmed the presence of divalent and trivalent iron in the precipitate (Fig. 5b). Divalent iron was initially derived from nZVI electro-dissolution and some of the divalent iron was then further oxidized to trivalent iron during the reaction. The O deconvolution spectra show the existence of the
peaks of –OH at 531.54 eV, lattice oxygen in metal oxides (O\(^2\)) at 530.74 eV, and chemically or physically adsorbed water (H\(_2\)O) at 532.91 (Fig. 5c) (Chen et al., 2018; Tan et al., 2018). The ratio of H\(_2\)O : –OH : O\(^2\) is 1.25 : 1.31 : 1. Nitrogen of NO\(_3\) is too low to be detected by XPS in this study.

Fig. 5 XPS spectra of the surface elements of the precipitate: a) survey spectrum; b) Fe element; c) O element.

3.3 Tafel, CV, and EIS analysis
Tafel polarization, EIS and CV experiments were performed to gain insight into the anodic reaction behaviors. Fig. 6a shows that the covered area in the CV curve increases with the initial nitrate concentration while the initial pH has slight effect on the CV curves (data not shown). This indicates that electric field facilitates the accumulation of nitrate ions on the nZVI surface with a denser double layer and further enhances the interaction between nZVI and nitrate. Fig. 6b shows the effect of initial solution pH on the Tafel plots. The $E_{\text{corr}}$ values of nZVI are $-0.94$ V, $-0.55$ V, and $-0.68$ V at pH values of 3, 6, and 10, respectively. $E_{\text{corr}}$ of nZVI at near neutral (pH=6) has a highest value, and then $E_{\text{corr}}$ shifts to lower potentials at either acid (pH=3) or alkaline (pH=10) condition due to more vulnerable to anodic oxidation. The corrosion current densities are 5.98, 11.56, and 56.34 μA cm$^{-2}$ at different pH values (10, 6, and 3). Correspondingly, as shown in Nyquist diagram and its equivalent circuit (Fig. 6c), charge-transfer resistances ($R_{\text{ct}}$) of the nZVI anode in different pH values (10, 6, and 3) are 24.3, 17.9, and 14.6 Ω. The corresponding polarization resistances ($R_{p}$) at pH of 3 has the lowest value of 12.05 Ω compared to 22.96 and 15.74 Ω (at pH 10 and 6), which is consistent with the observation that nZVI at pH of 3 is more vulnerable to anodic oxidation. The increase in charge-transfer resistances ($R_{\text{ct}}$) of the nZVI anode concomitant with a decrease in corrosion current density along with an increase of pH value is indicative of depletion of the reducible species and anodic formation of nuclei of a ferrous hydroxide film responsible for the low Rct (Wang and Farrell, 2003). The degree of coverage of the iron surface with the iron (hydr)oxides film is likely to increase at the more positive
potential and higher pH value because penetration of more hydroxyl ions into inner part of the double layer (Foroulis, 1979).

**Fig. 6** a) Cyclic voltammetry curves for anode at the initial nitrate concentrations of (50 mg L\(^{-1}\), 100 mg L\(^{-1}\) and 500 mg L\(^{-1}\)); b) Tafel curves, c) Nyquist plot of of anode at different pH values (3, 6, and 10) (Insert: The equivalent circuit).

### 3.4 Mechanisms of electrochemical nitrate removal

The schematic mechanism of the electrochemical denitrification process with
magnetically fixed nZVI anode coupled with RuO$_2$-IrO$_2$/Ti plate is shown in Fig. 7. Superior reduction of nitrate with simultaneous electrochemical oxidation of intermediates enhanced removal efficiency and N$_2$ selectivity. First, the applied electric field facilitates the interaction between nZVI on anode and the negative ion of NO$_3^-$ because more nitrate ions pile up on the nZVI surface. Second, NO$_3^-$ is simultaneously reduced by the surface-adsorbed atom H* from self-produced hydrogen in water electrolysis process (Zhao et al., 2022). Third, ammonia oxidation on RuO$_2$-IrO$_2$/Ti plate under high voltage not only reduced the ammonia intermediates and promoted the nitrate reduction reaction to the positive direction because there are no obvious ammonia accumulation as shown in Fig. 3. Fourth, iron(III) hydroxide flocs produced in the course of nZVI coagulation also slightly contribute to the nitrate removal via adsorption as shown in the xps data with nitrogen and iron elements. Fifth, the presence of electric field is also beneficial to reduce further passivation on nZVI surface caused by species of iron (hydr)oxides (Luo et al., 2010). This demonstrated that the coupling of RuO$_2$-IrO$_2$/Ti electrode with nZVI as an anode has a significant improvement on nitrate removal and N$_2$ selectivity.

Fig. 7 The schematic mechanisms of electrochemical nitrate removal.
4 Conclusions

In summary, we propose and analyze the performance of the nZVI anode based electrochemical nitrate removal process coupled with ammonia oxidation function plate (RuO$_2$-IrO$_2$/Ti). For a bulk NO$_3^-$ concentration of 100 mg L$^{-1}$, the maximum nitrate removal efficiency and N$_2$ selectivity reach 94.6 % and 72.8 % in 5 h, respectively. Compared to nZVI dosage, the initial pH value and the applied voltage had a strong influence on the nitrate conversion. The incorporation of RuO$_2$-IrO$_2$/Ti electrodes not only improved the nitrate conversion but also the N$_2$ selectivity because ammonia oxidation reduces the intermediates and promotes reduction reaction. The applied electric field is beneficial to the convective migration of nitrate and passivation mitigation on nZVI surface. Additionally, endogenous reactive hydrogen (atom H*) from water electrolysis process and iron hydroxides flocs from anodic oxidation enhance the nitrate removal via reduction and adsorption. CV curves confirmed the accumulation of nitrate ions on the nZVI surface with a denser double layer and further enhancement the interaction between nZVI and nitrate. Tafel polarization and EIS analysis provide the illustration that lower charge-transfer resistance (14.6 Ω) and lower corrosion potential (−0.94 V) and together with a higher corrosion current density (56.34 μA cm$^2$) of nZVI anode facilitates higher nitrate removal efficiency and N$_2$ selectivity. Utilization of nZVI anode coupled with ammonia oxidizing function plate can be a promising feasible approach to achieve high nitrate removal and N$_2$ selectivity.
Acknowledgement

Financial supports for this work were provided the Fundamental Research Funds of Zhejiang Sci-Tech University (2020Q048), Open Foundation of State Environmental Protection Key Laboratory of Mineral Metallurgical Resources Utilization and Pollution Control (HB201909), and Hangzhou Chuan En Environmental Technology Co., LTD. Authors have full power to use these grants.
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Highlights:

► Electrochemical nitrate removal was performed on nZVI/RuO₂-IrO₂/Ti anode.

► High nitrate removal efficiency and nitrogen selectivity was achieved near neutral medium.

► Electro-denitrification activity and N₂ selectivity was evaluated under different parameters.

► The mechanisms were proposed based on physiochemical and electrochemical properties of anode.
Declaration of interests

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

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: