Electrochemical redox treatment of denitrification in coastal secondary effluent using Ti/IrO2 anode

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Abstract：

In northern coastal industrial park, inlet of the wastewater treatment plant (WWTP) had the characteristics of low carbon source and high chloride ion concentration, which resulted in its poor biodegradability. In this case, the experiment explored an electrochemistral method to remove nitrogen. Cathodic potential, Ti/IrO$_2$ was confirmed as the anode and -1.6V was taken as the potential in order to remove nitrate-N. The findings include: when the initial chloride ion was 2000 and 3000 mg/L, the effect on the removal difference of nitrogen was slight. When the electrolysis time was 60 min, ammonia-N was removed completely, nitrite-N concentration kept 1mg/L approximately. The ammonia-N removal efficiency went up with the increasing cathodic potential, and was completely removed in different water samples, but nitrate-N removal showed an opposite result. The production amount of nitrite-N was the least at -1.6V. As the pH increased, ammonia-N and nitrate-N's removal efficiency went up first and then down, the removal effect was the best at pH being 9, Nitrite-N was less influenced by pH. After optimizing the raw water sample, Nitrate-N and TN removal efficiency were significantly increased, but the

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nitrite-N almost kept constant.

1 Introduction

China has pulled the discharge standard of pollutant from WWTP up to a higher level. The discharge standard upgraded from Level 1B to Level 1A of Discharge standard of pollutants for municipal wastewater treatment (GB18918-2002) (Chinese national standard). Now many WWTPs in north china are required to meet a higher level to quasi-four standard. Therefore, they are facing the promotion of quasi-four standard. To meet the standard, there are a number of technical barriers to be tackled, one of which is how to lower the concentration of total nitrogen (TN) to 15 mg/L. Many WWTPs are facing the fact that they are lack in carbon sources (a indispensable substance), which causes the TN discharge hard to meet the discharge standard. Compared with municipal WWTPs, costal industrial park plants in north China are confronted with such complicated problems as complex influent quality, low concentration of carbon source and high nitrate-N and ammonia-N concentration. All of this makes it very difficult to meet the new discharge standard.

There is little research on denitrification of influent from coastal industrial park WWTPs. The groundwater level in coastal areas is high, leaking to sewage pipelines, which leads to a high chloride concentration in influent of WWTP, especially in rainy seasons. Its chloride ion concentration can reach up to 10000mg/L. It becomes a subject for many engineers and scholars to make full use of the existing high chloride-ion concentration instead of carbon source to remove nitrogen. Current research mainly focuses on the configured sample in the lab. However, there is little experiment on the factual wastewater sample with high chlorine and low carbon from coastal industrial parks WWTPs.

Two methods are often employed to treat this kind of water, biological and electrochemical denitrification. Since the former requires many carbon sources, the latter becomes a better alternative.

The transformation mechanism from ammonia-N and nitrate-N to nitrogen gas was not the same as different denitrification technology. Wang took photoelectrochemical technology to remove ammonia-N, and there was about 49.1% transformate efficiency of ammonia-N to nitrate-N，(Wang, et al., 2014). Ammonia-N was absorbed onto the electrode and then electrolyzed to nitrogen gas. For photocatalytic fuel cell (PFC), ammonia-N tended to be oxidized to nitrate-N instead of nitrogen gas (Yan et al., 2018). In neutral solution, ammonia-N is oxidized by hydroxyl radicals produced by dissolved oxygen in water instead of adsorbed on the electrode, but the reaction process is very slow (Daye et al., 2018). When chloride ion exists in the solution, ammonia-N can be oxidized to nitrogen gas or nitrogen oxides (Kwang-Wook et al., 2005; Kamai et al., 2017; Garcia-Segura et al., 2019). In the study of nitrate-N electrochemical reduction process, the nitrogen-containing substances could be removed well, and the ideal effect can be achieved (Wei et al., 2018). Taking Co_3O_4/Ti as the electrode, the nitrate-N removal efficiency reached 96% (Choi et al., 2016). For the electrode $Pd–Cu/\gamma Al_2O_3$, the selectivity of nitrate-N was about 80.37% (Yao et al., 2021), and many factors could influence the result. Taking zero valent iron as the reductant, the removal of nitrate reached 83.3%. For Pd-coated alumina pellets, the value was only 64%, and nitrite-N reduction efficiency was only 1% (Beltramea et al., 2020). In addition, many researchers explored much redox experiment. Under the optimal conditions, it had better nitrate-N reduction effect (Kim et al., 2019; Liu et al., 2019).

Some researchers conducted the experiments with the existence of chloride ion in solution, which can accelerate oxidizing ammonia-N (Zhou et al., 2016) and reducing nitrate-N and produce less nitrogenous byproduct (Yao et al., 2019). So during the electrochemical reaction, chloride ion concentration in solution cannot be neglected. The chloride ion not only increased the conductivity of solution, but also participated in electrochemical

reaction. This could oxidize the intermediate product (Zöllig et al., 2017) and nitrogen-containing substances (Ma et al., 2016; Ben-Asher et al., 2016; Iranildes et al., 2019). For those experiments, many were conducted in lab with configured solution. However, there were few denitrification experiments on complex, high chloride and low carbon source in wastewater of WWTP in industrial park.

The experiment conducted the denification test by electrochemical technology, and made full use of the characteristics of high chloride and low carbon source in tailwater from costal WWTP, and studied the rules of electrochemical denification under different electrode materials, cathode potential, chloride ion concentration and pH conditions. The findings provided references for application of electrochemical denitrification of high chloride and low carbon source tailwater from costal industrial park WWTP

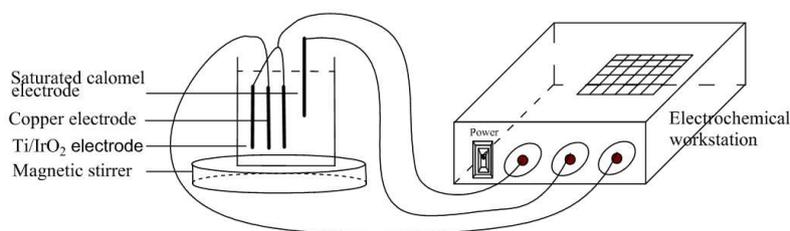# 2 Materials and methods

2.1 Electrodes and Apparatus

Fig. 1 Experimental apparatus diagram

The experimental apparatus diagram was shown as Fig.1 and adopted three-dimensional electrode. Cu (Shenzhen Yunding Metal Material Co., Ltd) was taken as cathode (Jiang et al., 2020), Ti/IrO$_2$ (Baoji Longsheng Nonferrous Metals Corporation) was the anode, and saturated calomel electrode (Shanghai Leici Electronic Technology Co., Ltd.) as the referenced anode. The electrode size was 5cm×6.5cm×0.1cm, the number ratio of cathode to anode is 2:1 and the effective chemical reaction area was 65cm^2 for each. Cu electrode was set between

the double Ti/IrO$_2$ electrodes and the space between the electrodes was 10mm. The equipment was made by polymethyl methacrylate with the size 5cm, 6cm and 12cm. Electrochemical work station (Tianjin Lanlike chemical and electricity high technology Co., Ltd) was used to adjust the cathode potential.

2.2 Experimental method and conditions

In the test, main monitoring items included TN, nitrate-N, nitrite-N, ammonia-N and pH. TN adopted the ultraviolet spectrophotometric method of potassium perchlorate oxidation. Nitrate-N and nitrite-N took ion chromatography methods. Nessler's reagent spetcrophotometry method was used to test ammonia-N. Chloride ion was prepared by sodium chloride, and KNO$_3$ and NH$_4$Cl were used for corresponding solution. All the chemicals were analytically pure and the experimental water was pure water. pH meter was Hach pH meter (HQ11d).

2.3 Sampling location

Raw tail water sampled from WWTP in Caofeidian new city of Tangshan Hebei China, and it is away 3km from Bohai bay. The water samples were taken in May dry season. In the dry season, it is less rainfall, and the groundwater leaks less into underground pipes. The chloride ion concentration in in tail water was relatively low. The chloride ion concentration in the sampled water this time was 1127 mg/L. In contrast, groundwater level in rainy season is high, more groundwater leaks into pipes, and the chloride ion in secondary effluent was about 2000 ~ 3000mg/L or even plus in daily monitoring. Due to the limitation of sampling time and space, the recording high value was about 10000mg/L. The sampled water quality parameters were as table 1.

Table 1 Water quality of wastewater treatment plant

parameters	COD$_{Cr}$ （mg/L）	pH	chloride ion （mg/L）	ammonia-N （mg/L）	nitrite-N （mg/L）	nitrate-N （mg/L）
value	66	7.3	1171	1.18	0.39	8.08

2.4 Experimental procedures

2.4.1 Linear volt-ampere curve

This experiment conducted in the solution with 25mg/L NO_3^-N and 0.1mol/L Na_2SO_4. Uniformly negative linear voltage was applied between -2.5V and 0V by an electrochemical workstation. The obtained curve is the linear volt-ampere curve.

2.4.2 Chloride electrolysis

In the experiment, cathode potential was set -1.6V, and the initial pH value of electrolyte was 7. In the configured water samples, the initial nitrate-N and ammnia-N was 20mg/L and 10mg/L, initial chloride ion was configured as 1000mg/L, 2000mg/L, and 3000mg/L respectively in different solutions. The aim was to investigate the effect of initial chloride ion concentration on denification.

2.4.3 Nitrogen removal test under different voltages

In order to explore the nitrogen removal effect, a proper cathodic potential should be got. Known from the linear volt ampere curve in Fig.3, the electrolytic current increased with applied voltage starting from 0V. The inflection point appeared when the cathode potential was about -1.1 V and then the current suddenly dropped. When the cathodic potential was -1.2V, a strong reduction appeared and it was the reduction peak of NO_3^-. Then, with voltage increasing from -1.2V, the current increased again. According to the characteristics of the linear volt-ampere curve, the proper potential should be chosen between -1.8V and -1.2V, and which would be taken as the cathodic potential of denitrification.
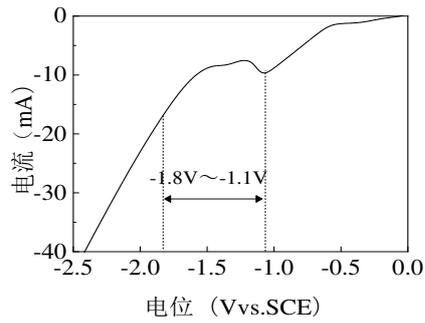
Fig. 2 Linear volt ampere curve

3. Results and discussion

3.1 Comparison of electrode materials

In the experiment, oxygen evolution was the main competitive side reaction and it affected the current efficiency. For chloride evolution, the chloride evolution over potential determined the efficiency of chloride evolution reaction, during the process, free chloride generated with strong oxidization and which oxidized ammonia-N. So the oxidation/chloride evolution should all be considered in the experiment. Oxygen/chloride evolution polarization curves of three different anode materials were measured in 0.5mol/L sodium sulfate and saturated sodium chloride solution, separately. According to the above analysis, the process for selecting proper electrodes were stated below.

Three electrodes were used to conduct the experiment. Known from Fig.2, Ti/RuO_2-SnO_2 has the smallest difference value between oxygen/chloride evolution comparing with that of other two materials. And the value was 0.45V. The oxygen evolution was the lowest. In the electrochemical reaction, competitive adsorption of OH^- and Cl^- happened on electrode surface. The smaller of the potential difference, the more the oxygen evolution side reaction occurred and the more current was used for oxygen evolution. This reduced the current efficiency for ammonia-N

removal. The oxygen/chloride evolution of Ti/RuO$_2$-IrO$_2$ (Zhi et al., 2020;) ranked the second with value 0.50V, but the chloride evolution was the highest 0.98V. For instance, if the chloride evolution was too high, it would increase the voltage of reaction tank and energy consumption would increase accordingly. The voltage difference of Ti/IrO$_2$ was the biggest 0.56V with the lowest chloride evolution. The oxygen evolution was among two other electrodes. When the voltage difference of oxygen/chloride evolution was large and it would reduce the generation of side reaction. The lower the chloride evolution was, the easier the free chloride being produced. Thus, the ammonia-N removal efficiency improved. So taking Ti/IrO$_2$ as anode material was more suitable than the other two ways in this research. Ti/IrO$_2$ became the most appropriate anode with these advantages, such as highly conducting, physically hard and chemically stable and inert.
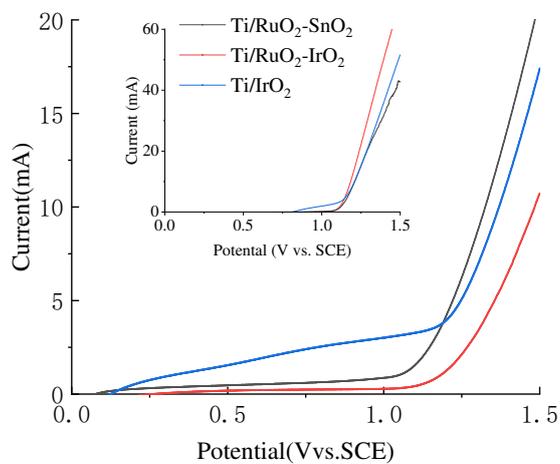

Fig. 3 Oxygen/chlorine evolution polarization curves of three electrodes (the imbedded figure is the chlorine evolution curve, the large figure is the oxygen evolution curve)

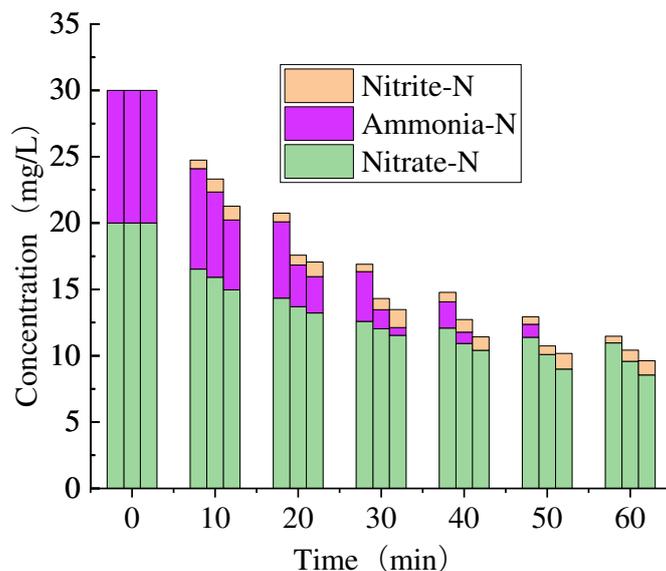## 3.2 Nitrogen removal under different chloride ion concentration

Fig. 4 Effect of different chloride ion concentration on nitrogen removal

(The initial nitrate-N and ammonia-N concentration in Fig. 4 were 10, and 20 mg/L, respectively. In each three-data-group in the seven time points, ammonia-N, nitrite-N and nitrate-N were tested with the chloride ion 1000, 2000, 3000 mg/L from left to right.)
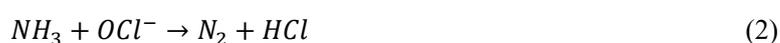
Seen from Fig. 4, nitrate-N and ammonia-N concentration decreased gradually with the prolonging of electrolysis time. Nitrite-N came to appear within 10 min. Ammonia-N was not detected for the first time at the chloride ion concentration 3000mg/L and the time 40 min. Electrolysis time 50min and chloride ion concentration 2000mg/L, ammonia-N was all removed. All the ammonia-N was removed when the time lasted 60min. The removal effect of ammonia-N was mainly caused by free chloride. With the promoting of chloride ion in solution, the producing amount of free chloride would increase accordingly, so the oxidation efficiency of free chloride on ammonia-N became higher. The reaction was just depicted as formula (1)~(2).
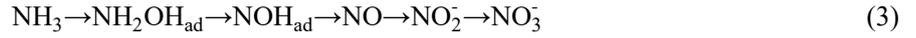
For nitrite-N, its concentration was about 1mg/L when the time 10 min, and there was no obvious change after that time. In this case, the concentration of nitrate-N had a little effect on the nitrite-N concentration. The effect

occurred during the transformation of nitrogen gas from nitrate-N, part of which turned into nitrite-N ((Choi et al., 2016)). Nitrite-N as the intermediate product was a non-negligible product produced during the transformation from nitrate-N to nitrogen gas. This agreed on previous peers (Rao et al., 2019; Dash et al., 2005). During the electrolysis, ammonia-N also might transform to nitrite-N or further into nitrate-N, just as formula (3), but there is no effect on the existence of nitrite-N. Based on this, when the ammonia-N was all oxidized, the nitrite-N still kept the constant value (Ma et al., 2020). But the whole process should be verified in more experiments.

The increase in chloride ion concentration and prolonged electrolysis time, allowed the removal efficiency of ammonia-N and nitrate-N to go up. The total concentration of the three nitrogen-containing substances decreased. The transformation process was shown in formula (4) ~ (7)，nitrate-N was reduced to nitrite-N and nitrogen gas, and nitrite-N was also reduced to nitrogen gas or ammonia-N (Kuang et al., 2020; Zhang et al., 2021). When the chloride ion concentration was 2000 and 3000mg/L, the concentration difference with different electrolysis time was small. But with the chloride ion concentration 1000mg/L, the sum of three nitrogen-containing substances concentration was obviously higher than the other two. However, it was opposite with the time 60min. Within 60min, the total concentration of three nitrogen-containing solutions was all lower than 15mg/L. That could be explained by that appropriate chloride ion dosage was beneficial for the removal of nitrite-N. Furthermore, different nitrate concentration corresponded to different proper chloride ion dosage. According to the analysis and Fig. 4, there is no obvious difference in the nitrogen-containing removal under different chloride ion concentration. Therefore, the chloride ion concentration was configured 2000 mg/L in the following experiment.

The proposed reaction formula shown as followed (Kim et al., 2005; Ji et al., 2021; Moura et al., 2005):

$$Cl^- \rightarrow Cl_2 \rightarrow HOCl \rightarrow OCl^- \tag{1}$$

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

$$NH_3 \rightarrow NH_2OH_{ad} \rightarrow NOH_{ad} \rightarrow NO \rightarrow NO_2^- \rightarrow NO_3^- \tag{3}$$

$$NO_2^- + H_2O \rightarrow NH_3 + OH^- \tag{4}$$

$$NO_2^- + H_2O \rightarrow N_2 + OH^- \tag{5}$$

$$NO_3^- + H_2O \rightarrow NH_3 + OH^- \tag{6}$$

$$NO_3^- + H_2O \rightarrow NO_2^- + OH^- \tag{7}$$

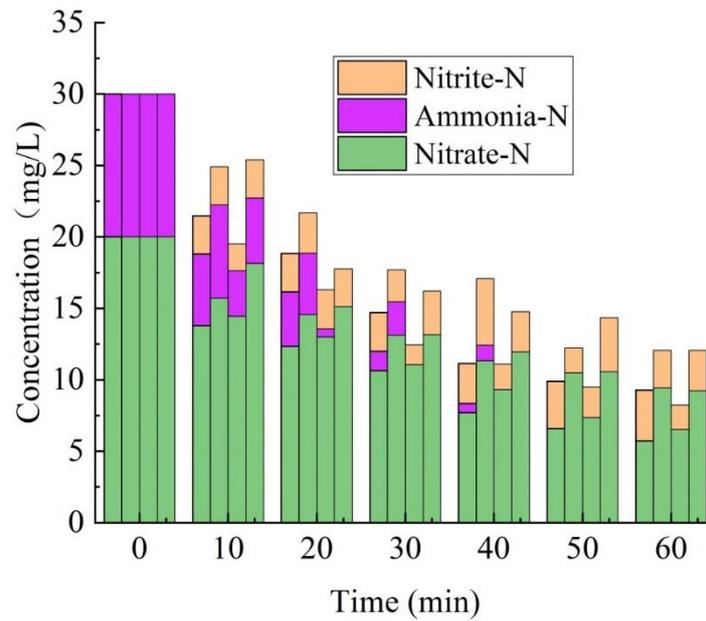## 3.3 Effect of cathode potential on nitrogen removal

Fig. 5 Effect of cathode potential on nitrogen removal

（In Fig. 5, the initial ammonia-N and nitrate-N concentration was 10, and 20 mg/L respectively. In seven time points, the test was conducted. Four sets of data formed a time point group, and in each group, ammonia-N, nitrate-N and nitrite-N were measured under the cathodic potential -1.2, -1.4, -1.6, -1.8V from left to right.）

Known from Fig. 5, nitrite-N and ammonia-N concentration decreased gradually with time prolonged.

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Nitrate-N turned up for the first time in the four water samples within the time 10 min. In the following process, there was no obvious concentration difference under different cathodic potential.

With the increase of cathodic potential, removal efficiency of ammonia-N increased gradually and the best removal efficiency appeared at -1.8V. When it was 10min, ammonia-N could not be detected. The followed potential order was -1.6V and -1.8V. But for the potential -1.2V and -1.4V, the removal efficiency was lower and removed completely within 50min. The main reason was that the increasing cathodic potential allowed cell voltage to increased, which led to increased current density on unit area, more electrons transferred, more free chlorine. Then the free chlorine reacted with ammonia-N, which showed faster removal efficiency. The result was similar to Guo Di's research (Guo et al., 2016).

In terms of nitrate-N removal, the removal efficiency was the best when the cathodic potential was -1.2V and it was 71.42% within 60min. This was consistent with the linear volt-ampere curve above. The reduction peak occurred at -1.2V. Next, when the cathodic potential was -1.6V, the removal efficiency was 67.4%; but for -1.8V, the efficiency was the lowest. This could be explained as the fact that the negative potential shift intensified the occurrence of hydrogen evolution reaction. And the increased hydrogen evolution reaction produced more bubbles, which not only reduced the adsorption area, but also led to the competitive adsorption of H+ and NO_3^-. This, therefore, reduced the current efficiency and affected the removal efficiency.

The formation of nitrite-N as depicted in Fig. 5, under different cathodic potential, nitrate-N concentration increased faster within the first 10 min, and reached 2~4 mg/L, but It fluctuated up and down in a certain range after 10min. when the cathodic potential was -1.6V, it produced relatively little nitrite-N. which as the intermediate produce produced during the reduction process from nitrate-N to nitrogen gas, the cathodic potential was less selective to its formation. It also showed that, nitrite-N was a noteworthy factor affecting the removing of nitrate-N.

An interesting phenomenon could be seen from the above analysis and Fig. 5. During the electrolysis process, when the cathodic potential was -1.6V, the three nitrogen-N substances— ammonia-N, nitrate-N and nitrite-N all achieved the highest removal efficiency 82.3%. The value was better than that in the reduction peak potential -1.2V, and the selectivity of nitrogen generation was higher at this time. At the same time, it was very important to choose appropriate cathode potential for electrochemical denitrification. If the cathode potential was too low, the current density was relatively low, the catalytic effect was not satisfactory, and the removal efficiency also decreased. If the cathode potential was too high, the hydrogen evolution reaction would be violent, affecting the nitrate-N removal efficiency. So, in the following experiment, -1.6V was chosen as the cathodic potential.

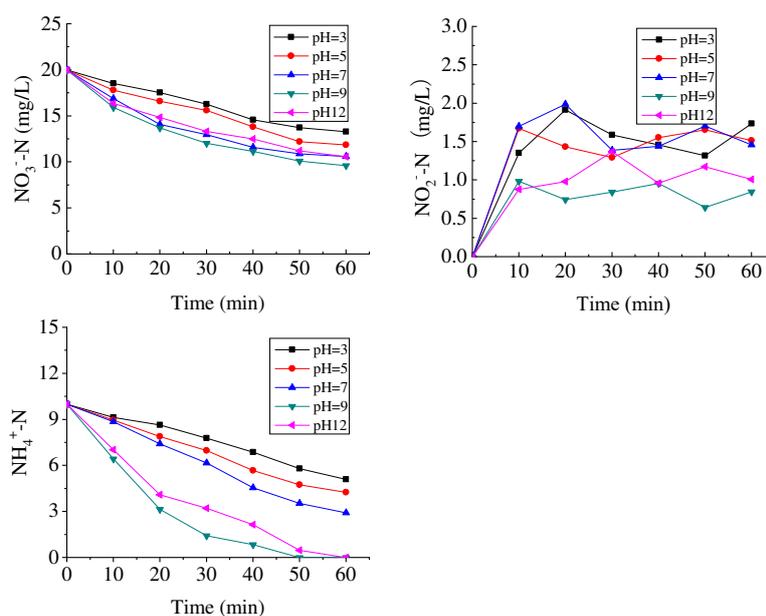## 3.4 Nitrogen removal under different pH conditions

Fig. 6 Nitrogen removal and variation of pH in solution under different pH conditions

Seen from Fig. 6, initial pH value in solution had great affect the on the removal efficiency of ammonia-N. When the pH was 3, the removal efficiency of ammonia-N was the lowest with the time 60 min and the value was 48.8%. The removal efficiency increased with the increase in initial pH value. When the initial pH equaled 9 and

the time was 50min, ammonia-N could not be detected in the solution. Then, with the increasing pH value, the removal efficiency slowed down. When pH was 12 and the time was 60min, ammonia-N was removed completely, and the efficiency was better than that when the pH value was 3, 5, and 7, respectively. The phenomenon was that, the removal efficiency of ammonia-N gradually increased and then slowed down with the pH value increasing. This suggested that the removal efficiency of ammonia-N under weak alkali condition was higher than that under strong alkali and acid conditions (Yao et al., 2016). Under the acidic conditions, ammonia-N mainly exists in the form of NH_4^+, which is not easy to be oxidized compared with NH_3. Moreover, Cl_2 overflows easily and free chloride concentration reduces. Under the condition of strong alkali, there is a large amount of OH^- in solution, which will diffuse to the anode during electrolysis process and adsorb competitively with Cl^-. In addition, OH^- reacts with free chloride forming ClO_3^-, which hinders the oxidation of ammonia-N. This is consistent with the conclusion of Qin Jingjing ((Qin, 2016)).

When initial pH was 3, the removal efficiency of nitrite-N was the lowest, only 33.6%. When the initial pH was 9, the best removal efficiency reached 52.1%. However, with pH 12, the efficiency dropped. This was, to some extent, different from Ding Jing and Zhang Dongmei's research. Dingjing thought the effect of pH on the removal of nitrate-N was not obvious (Ding, 2016). Differently, Zhang Mei believed it was beneficial to nitrate-N reduction when the initial pH was low (Zhang, 2013). Their different opinions consisted in the decreasing H^+ concentration gradually with the increasing pH. According to formula(1), there is a dynamic equilibrium between OCl^- and H^+: the OCl^- concentration went down, weakening the oxidation of OCl^- on ammonia-N and other nitrogen-containing substances. The removal efficiency of nitrate-N went up. When the pH was higher, the competent absorption between OH^- or other substances and H^+ occurred on the electrode, which hindered the removal of nitrate-N. The removal efficiency of nitrate-N increased with the increasing pH.

To some extent, the production of nitrite-N was affected by pH value, but the effect was slight. In the first 10min, the nitrite-N concentration went up quickly, and then fluctuated within a certain range, and the concentration value kept between 0.8 and 1.6 mg/L. The lower pH, the less the produced nitrite-N. When the initial pH was 9, the amount of nitrite-N was the least. Under weak alkali condition it was lower than that under strong alkali and acid condition. The effect of nitrite-N removal rule was familiar to that of ammonia-N. Further research is expected in the effect of pH on nitrite-N removal.

3.5 Nitrogen removal efficiency in raw and optimized raw water

Fig. 7 depicted the denitrification effect of electrolyzed wastewater samples under different conditions. After 60 mins' electrolysis, it could be seen that the concentration of nitrogen-containing substances showed a downward trend, and the removal efficiency of the optimized wastewater was significantly higher than that of the wastewater without optimization. Under the optimal conditions, the reduction rate of nitrate-N was more quickly, and the removal efficiency was 56.93% and 71.41% respectively before and after optimization. Under the condition of optimal raw water parameters, the org-N removal efficiency was much higher than that of raw water. The nitrite-N concentration increased and stayed at a certain level. In contrast, the concentration of the optimal raw water maintained and showed no obvious change under the optimized operating parameters. This might attribute to the faster oxidization of nitrite-N caused by increasing Cl^- concentration. Ammonia-N was not detected during the electrolysis, because its concentration was rather low, 1.18mg/L and it had been completely oxidized in a short time. This fact was contrary to the research whose conclusion was that ammonia-N increased first and then decreased while nitrite-N was not detected (Shen, 2020). The TN decreased quickly under the optimal parameters with its concentration 3.87mg/L in 60 min and the removal efficiency being 71.2%. In summary, the optimal operational parameters were better than that or raw water and better electrolysis denitrification. It was consistent with the

prepared wastewater results. That is to say, the chloride ion concentration in rainy season is much higher than other seasons, the electrochemical denitrification efficiency is better, and the tests is supposed to be carried out in the future experiments.
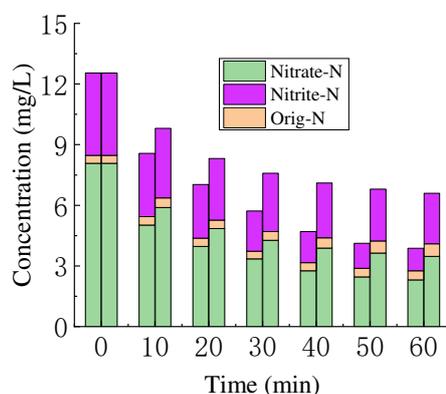

Fig. 7 Concentration changes of org-N, nitrite-N, nitrate –N and TN under different conditions（in each group, it was the optimal and raw water sample from left to right）

4 Conclusions

The research conducted the electrochemical denitrification in the tailwater, simulated and optimal tailwater. Tailwater sampled from WWTP of costal industrial park and it had the characteristics of high chloride and low carbon resource. The following conclusions were drawn.

The concentration of initial chloride ion concentration 2000 and 3000mg/L made no obvious difference to the nitrogen removal. Ammonia-N was completely removed in 60min, and the nitrite-N concentration was about 1mg/L. In the course of experiment, with the increasing cathodic potential, the removal efficiency of ammonia-N went up gradually, ammonia-N in different water samples were completely removed completely in 50 min. by comparison, the conclusion on nitrate nitrogen was opposite. When the cathodic potential was -1.2V, the highest efficiency was 71.4% and the nitrite-N amount was the least at -1.6V. For -1.6V, pH had great influence on the

removal of ammonia-N: with the increase in pH, the removal of ammonia-N and nitrate-N increased firstly and then decreased. The best result appeared at pH being 9, nitrite-N was less affected by pH value. By comparing the raw and optimized raw water samples, the reduction efficiency of nitrate-N in optimized raw water increased from 56.9% to 71.4%, nitrite-N concentration kept constant, and TN removal efficiency also increased significantly.

Ethics approval

Not applicable

Consent to Participate

Informed consent was obtained from all individual participants included in the study.

Consent to Publish

Not applicable.

Credit authorship contribution statement

Yaozong Zhang: Conceptualization, Methodology, Software, Investigation, Writing -original draft. **Bo Pang**: Validation, Formal analysis, Visualization, Software, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no competing interests

Acknowledgements

Data Availability Statement

The datasets used and/or analysed during the current study are available from the corresponding author on

reasonable request.

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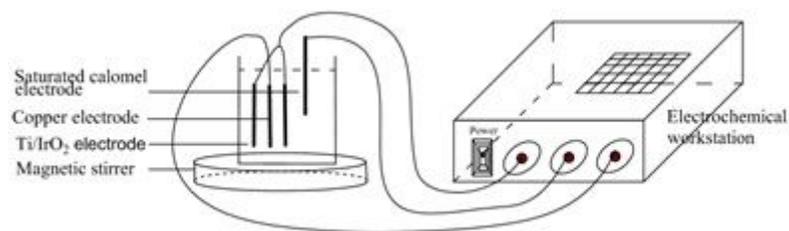
Figures

Figure 1

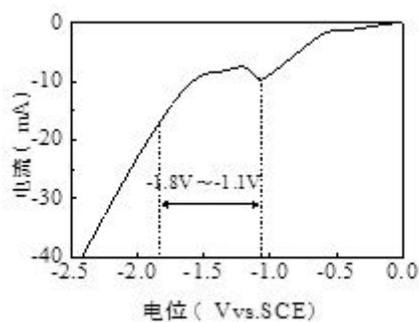Experimental apparatus diagram

Figure 2
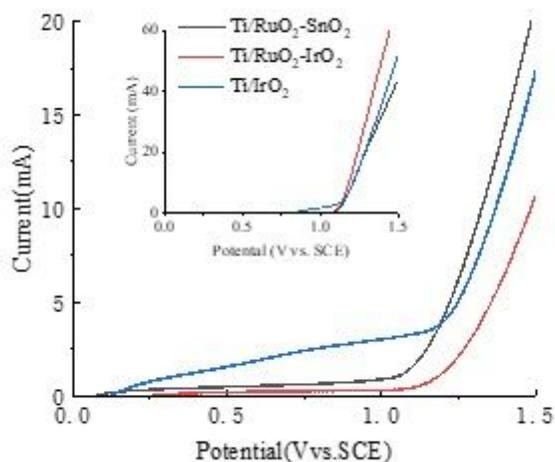
Linear volt ampere curve

Figure 3

Oxygen/chlorine evolution polarization curves of three electrodes (the imbedded figure is the chlorine evolution curve, the large figure is the oxygen evolution curve)
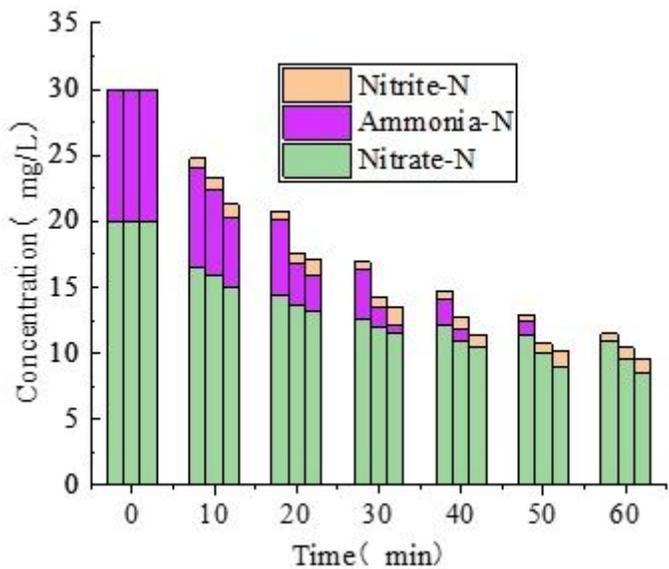
Figure 4

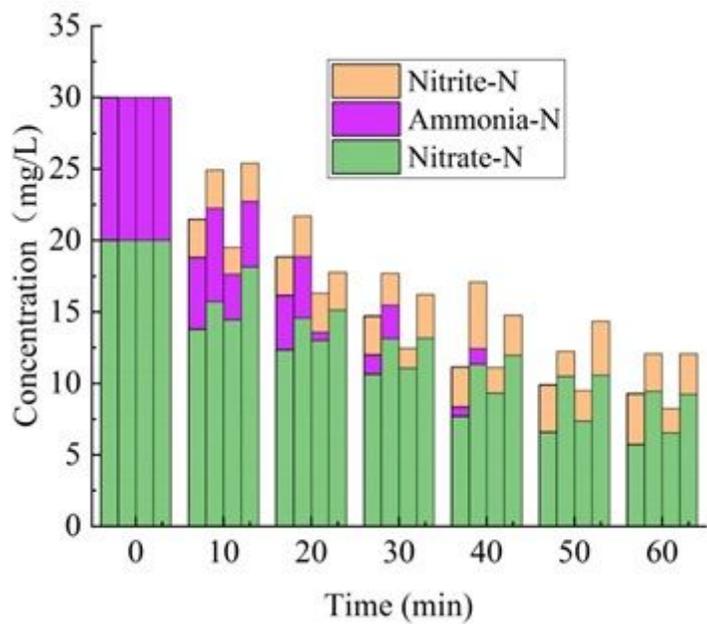Effect of different chloride ion concentration on nitrogen removal

Figure 5

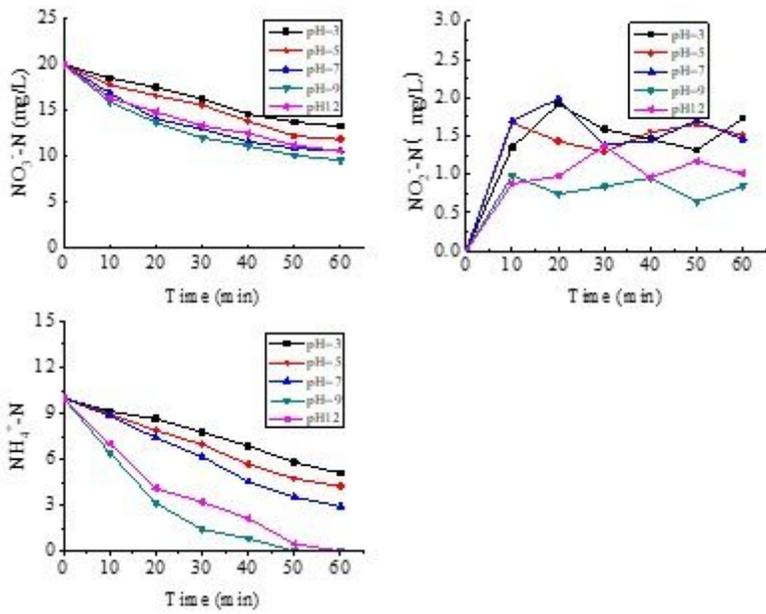Effect of cathode potential on nitrogen removal

Figure 6

Nitrogen removal and variation of pH in solution under different pH conditions
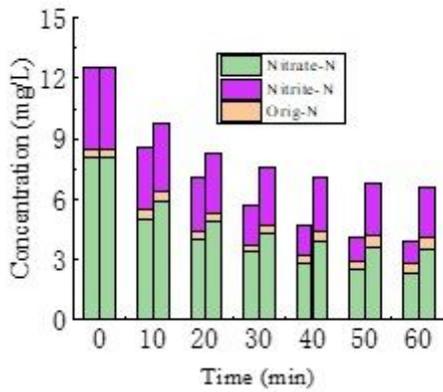

Figure 7

Concentration changes of org-N, nitrite-N, nitrate −N and TN under different conditions（in each group, it was the optimal and raw water sample from left to right）