Application of Pd-Sn modified Ru-Ir electrode for treating high chlorine ammonia-nitrogen wastewater

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ABSTRACT
Electro-catalytic technology is a promising approach for wastewater treatment, owing to its easy operation, minimal generation of secondary pollution, small foot-print and rapid start-up. In this work, the chlorine evolution potential of the Pd-Sn modified ruthenium(Ru)-iridium(Ir) electrode was investigated for the electro-catalytic treatment of high chlorine ammonia-nitrogen wastewater. The effect of reaction conditions on the removal of ammonia-nitrogen, kinetics and apparent activation energy of ammonia-nitrogen removal were studied. The possible denitrification process of high chlorine ammonia-nitrogen wastewater was discussed. The results indicated that the chlorine evolution potential of the Pd-Sn modified Ru-Ir electrode was 1.0956 V (vs. SCE). The electro-catalytic treatment of high chlorine ammonia-nitrogen wastewater conformed to zero-order kinetic law, and the apparent activation energy of removal process was 14.089 kJ/mol. With a current of 0.5 A, the removal efficiency of ammonia-nitrogen could achieve 100% at a reaction time of 40 min. Indirect oxidation played an essential role in the electro-catalytic ammonia-nitrogen removal using the Pd-Sn modified Ru-Ir electrode. This paper demonstrated that the electro-catalytic technology was a promising approach for efficiently treating the high chlorine ammonia-nitrogen wastewater.

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1. Introduction
Ammonia-nitrogen wastewater generated from complex refinery and chemical enterprises is detrimental to the environment, as they can cause not only an offensive smell, but also eutrophication that is fatal to aquatic life. The high salt and high ammonia-nitrogen wastewater with poor biodegradability is often characterized as high ammonia-nitrogen concentration of 50–200 mg/L and high salt content (calculated by chloride ion) of 1.0–25.59 g/L [1–3]. Therefore, it is difficult for traditional sewage treatment plants to treat this wastewater, which increases the huge pressure of environmental control and economic cost of the refinery, and causes potential danger to the environment.

The commonly used technologies for treating ammonia-nitrogen wastewater mainly include biological degradation [4–13], physical–chemical method [14–16], physical adsorption [17,18], advanced oxidation [19–23], and chemical precipitation [24–27]. These technologies have great constraints for treating high chlorine ammonia-nitrogen wastewater. Biological methods for treating ammonia-nitrogen wastewater rely largely on microorganisms, which have stringent requirements for environmental conditions, such as wastewater toxicity, C/N ratio, salt concentration, and operational parameters [28]. However, high chlorine ammonia-nitrogen wastewaters are easy to dehydrate microorganisms, making them lose the cell activity and integrity. Advanced oxidation technologies, such as ultrasonic and photocatalysis, usually require high costs, high...
energy consumption and complex operational skills. With respect to adsorption technology, there are a variety of competitive ions that can form adsorption with ammonia-nitrogen in the high chlorine ammonia-nitrogen wastewater, resulting in poor removal efficiency of ammonia-nitrogen. What is more, it is difficult to achieve the desorption of the adsorbent itself. Chemical precipitation uses chemical substances containing magnesium compounds and phosphate to remove the ammonia-nitrogen. This method will consume a large number of magnesium compounds and phosphorus-containing substances, but the reaction is not complete, which will release a large amount of phosphorus into the environment, causing re-pollution of water bodies.

Electro-catalytic technology has attracted increasing attention as a promising approach for wastewater treatment, owing to its easy operation, minimal generation of secondary pollution, remote control, a wide range of operating temperature, rapid start-up, small foot-print, and high removal efficiency of contaminants [29,30]. In particular, electrochemical processes exhibit a superiority in eliminating nitrogenous contaminants to biological processes since \( \text{NH}_4^+ \) is readily oxidized at the anode while nitrates and nitrites can be reduced at the cathode [31]. At the same time, hydrogen is produced on the cathode, which can be collected as an energy source. Although electrochemical technology has the disadvantage of high power consumption, compared with physical, chemical, and biological technologies, it exhibits superiority in the treatment of ammonia-nitrogen wastewater with high toxicity, poor biodegradability, and high salt content.

As one of the major mechanisms for electrochemical ammonia removal from wastewater, direct anodic oxidation proceeds via sequential dehydrogenation of adsorbed ammonia on electrode surfaces when a sufficiently positive potential was applied to the electrode. Therefore, electrode materials are the key factors in treating the high chlorine ammonia-nitrogen wastewater by electro-catalytic technology. The majority of research on the direct oxidation of ammonia has been carried out using platinum (Pt) [32]. The modification of Pt catalysts with other electrode materials, such as Ti/\( \text{SnO}_2 + \text{Sb/PbO}_2 \), has been well documented for the efficient removal of ammonia-nitrogen in coking wastewater [33]. Electrochemical technology using \( \text{Ti/RuO}_2 - \text{IrO}_2 \) as an anode can synergically remove total ammonia-nitrogen (TAN) and nitrite in circulating aquaculture wastewater [34]. The \( \text{SnO}_2 \) electrode is found to be efficient for the removal of organic matter, however, its lifespan is short; Similarly, toxic Pb can be dissolved from the \( \text{PbO}_2 \) electrode, resulting in secondary pollution of wastewater.

The \( \text{RuO}_2 - \text{IrO}_2 \)-based catalyst is considered as an excellent electrode material in terms of ammonia oxidation, owing to its stability, high electrical conductivity, and excellent chlorine-evolution performance [35]. However, the \( \text{RuO}_2 - \text{IrO}_2 \) electrode has relatively poor corrosion resistance, and its service life is still short in industrial practical application. By contrast, Pd is more cost-effective, and has better corrosion resistance, compared to Pt. \( \text{Pd-SnO}_2/C \) has been reported to exhibit good electrical conductivity and electro-catalytic performance [36]. With this regard, the modification of the Ru-Ir electrode with Pd-Sn has been explored by combining the catalytic performance of Sn and corrosion resistance of Pd, to significantly enhance the electro-catalytic performance of the Pd-Sn-based catalyst derived from the Ru-Ir electrode. However, the effect of modification of the Ru-Ir electrode with Pd-Sn on electro-catalytic treatment of high chlorine ammonium-nitrogen wastewater has not been studied.

Furthermore, reaction conditions can affect the performance of electro-catalytic ammonia-nitrogen in the process of electro-catalytic oxidation of the high chlorine ammonia-nitrogen wastewater. In general, the main factors affecting the industrial application of electro-catalytic treatment of high chlorine ammonia-nitrogen wastewater include chloride ion concentration, initial concentration of ammonia-nitrogen, current, voltage, electrode material, \( \text{pH} \), temperature, types and content of organic matter, suspended matter, etc [37–39]. For instance, Ma et al. prepared the Ti/\( \text{SnO}_2 + \text{Sb/PbO}_2 \) anode to investigate the effects of operating parameters including current density, anode material, \( \text{pH} \), and the concentration of chloride by the orthogonal array experimental design and reported that the anode material, current density, and chloride concentration have significant influences on ammonia removal [33]. Kim et al. evaluated the effects of the \( \text{pH} \) and the chloride ion in the solution and kinds of anodes on the electrolytic decomposition of ammonia and revealed that the performances of the electrode was totally in the order of \( \text{RuO}_2 > \text{IrO}_2 > \text{Pt} \) in both the acid and alkali conditions and the ammonia decomposition was the highest at a current density of 80 mA/cm\(^2\) [40]. Furthermore, the Ti/\( \text{RuO}_2 - \text{IrO}_2 \), the Pt/ITO electrode, and the BDD anode were also applied to the treatment of ammonia-nitrogen wastewater [41–43]. However, the effect of chloride ion concentration, \( \text{pH} \), and temperature on the electro-catalytic treatment of high chlorine ammonia-nitrogen wastewater by the Pd-Sn modified Ru-Ir electrode remains largely unknown.
This paper is aimed to evaluate the electro-catalytic effect of the modification of the Ru-Ir electrode with Pd-Sn on treating high chlorine ammonia-nitrogen wastewater. More specifically, this study is aimed to (1) investigate the chlorine evolution performance using the modification of the Ru-Ir electrode with Pd-Sn; (2) evaluate the influence of operational conditions on the removal of ammonia-nitrogen, kinetics and apparent activation energy; and (3) explore the possible denitrification process in the electro-catalytic treatment for high chlorine ammonia-nitrogen wastewater.

2. Experiment

2.1. Chemicals and materials

Sodium chloride (NaCl, 99.5%), palladium chloride (PdCl2, 99%), stannous chloride pentahydrate (SnCl2·5H2O, 99%), and ruthenium(III) chloride hydrate (RuCl3·xH2O, 98%) were purchased from ALADDIN Reagent (Shanghai) Co., Ltd. Anhydrous ethanol (C2H6O, 99.5%) was bought from Shanghai Macklin Biochemical Co., Ltd. The titanium (Ti) matrix and Ru-Ir electrode were obtained from Baoji Zhong Tai Material Co. Ltd. The titanium (Ti) matrix and Ru-Ir electrode were obtained from Shanghai Macklin Biochemical Co., Ltd. The titanium (Ti) matrix and Ru-Ir electrode were obtained from Baoji Zhong Tai Material Co. Ltd.

2.2. Preparation of modified Ru-Ir electrodes with Pd-Sn

Ruthenium trichloride, iridium tetrachloride, palladium chloride, and tin tetrachloride were mixed with an appropriate amount of polyethylene glycol in a beaker containing 10 mL deionized water with the mole Ru-Ir ratio of 2:1, the mole Pd-Sn ratio of 3:1. Besides, the mass of Pd-Sn accounted for 1.5% of the total mass of the elements. After oscillating in an oscillator for 2 h, the solution was sonicated in an ultrasonic instrument for 1.5 h (40°C, 45 kHz). Thereafter, it was oscillated in the oscillator for another 30 min to completely dissolve the active material.

In order to modify Pd-Sn with the Ru-Ir electrode, the Ti plate (5.4 cm × 5.0 cm × 0.2 cm) was polished using coarse and fine sandpaper. After a metallic lustre was observed, the Ti plate was put into 10% sodium hydroxide solution and heated at 100°C for 2 h, followed by 10% oxalic acid for 2 h’s mild boiling treatment. Then 0.1 mL of the precursor solution of the modified Ru-Ir electrode with Pd-Sn was added to the etched Ti plate each time. The solution on the surface of the electrode was kept flat. After natural drying, the solution was dried in the oven at 105°C for 5 min and then placed in the muffle furnace for thermal oxidation at 500°C for 15 min. The impregnation, drying, and thermal oxidation were repeated for 15 times. Thereafter, it was kept at a constant temperature of 500°C in a muffle furnace for 4 h, and then naturally annealed to room temperature. In this way, a modification of the modified Ru-Ir electrode using titanium-based Pd-Sn was well prepared, with catalyst content of 15 mg/cm² (based on the total mass of elements).

2.3. Experimental setup and procedure

The experiment was carried out in a 210 mL special electrolytic cell with the introduction of 200 mL high chlorine ammonia-nitrogen wastewater. The electrode dimension was 5.4 cm × 5.0 cm × 0.2 cm. The Pd-Sn modified Ru-Ir electrode was used as the anode, while the platinum electrode was used as the cathode. The anode and cathode electrodes were spaced 4 cm apart and placed parallel in the electrolytic cell. The wastewater was stirred with a magnetic stirrer (700 rpm), and a DC Power Supply (DH1718E-5 DC Power Supply) was used to provide the required current and voltage. Hydrochloric acid and sodium hydroxide were used to adjust the initial pH (3, 5, 7, 9, 11), while sodium chloride was used to adjust the concentration of chloride ions (1000, 3000, 5000, 7000, 10,000 mg/L). A thermostatic water bath was used to maintain the temperature (30°C, 40°C, 50°C, 67°C, 78°C) of the reaction solution.

The removal rate of ammonia-nitrogen as an index, the effects of reaction conditions on ammonia-nitrogen removal were studied, and the kinetic and apparent activation energies were investigated. The possible denitrification pathway of ammonia-nitrogen was discussed by measuring the products of the ammonia-nitrogen removal process.

2.4. Analytical methods for electrochemical performance

The linear sweep voltammetry (LSV), the cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were measured by an electrochemical workstation (CHI660E Shanghai Chenhua Instrument Co., Ltd.) with a three-electrode system. In saturated sodium chloride, the LSV of the Pd-Sn modified Ru-Ir electrode was used to observe the change in the chlorine evolution potential of the electrode. The CV and EIS of the Pd-Sn modified Ru-Ir electrode were measured in the simulated high chlorine ammonia-nitrogen wastewater.

2.5. Analytical methods for water quality

The pH of wastewater was measured with a pH metre. The temperature was measured using a thermometer.
The concentrations of NH$_3$-N, NO$_3$-N and NO$_2$-N were determined by a gas phase molecular absorption spectrometer (GMA3378), while the TN level was measured using a liquid phase total organic carbon analyzer (TOC-VCPH).

High performance liquid chromatography (HPLC) coupled with a LC-10AT vacuum degassing pump, a DGU-12A quaternary pump, a SIL-10AD autosampler, and a fluorescence detector (Japan Shimadzu RF-10AXL), was used to measure the contents of 2,3-dihydroxybenzoic acid and 2,5-dihydroxybenzoic acid, in order to determine the concentration of hydroxyl radical. HPLC included the separation which was achieved using a XDB-C18 chromatographic column (5 μm × 4.6 mm × 150 mm). The mobile phase was set up using 3% acetic acid solution–methanol (75:25, v/v) at the flow rate of 1.0 mL/min, and the injection volume was 10 μL at temperature of 30°C.

3. Results and discussions
3.1. The chlorine-evolution performance

Figure 1 presents a comparison of the chlorine evolution potential between the unmodified Ru-Ir electrode and the modified Ru-Ir electrode with Pd-Sn using a saturated calomel electrode (SCE) as a reference electrode in the saturated sodium chloride solution. The chlorine evolution potentials of the unmodified ruthenium-iridium electrode and the Pd-Sn modified Ru-Ir electrode were 1.1663 and 1.0956 V, respectively. The chlorine evolution potential of the Pd-Sn modiﬁed Ru-Ir electrode was lower than that of the unmodiﬁed electrode, indicating that the Pd-Sn modiﬁed Ru-Ir electrode exhibited a better chlorine evolution performance. At 1.3 V, the current of the unmodified Ru-Ir electrode and the Pd-Sn modiﬁed Ru-Ir electrode were 0.0040 and 0.2373 A, respectively, indicating that the conductivity of the Pd-Sn modiﬁed Ru-Ir electrode in saturated sodium chloride was better than that of the unmodiﬁed Ru-Ir electrode. Previous studies indicated that the following chemical reactions may occur in the electro-catalytic treatment of wastewater containing chlorine and ammonia-nitrogen [44,45]:

\[
\begin{align*}
\text{Cl}^- & \rightarrow \cdot\text{Cl} + e^- \\
2\text{Cl}^- & \rightarrow \text{Cl}_2(aq.) + 2e^- \\
\text{MO}_x + \text{H}_2\text{O} & \rightarrow \text{MO}_x(\cdot\text{OH}) + \text{H}^+ + e^- \\
\text{MO}_x(\cdot\text{OH}) + \text{Cl}^- & \rightarrow \text{MO}_x(\cdot\text{OCl}) + \text{H}^+ + 2e^- \\
\text{MO}_x(\cdot\text{OCl}) + \text{Cl}^- & \rightarrow \text{MO}_x + \text{Cl}_2(aq.) + e^- \\
\text{Cl}_2(aq.) + \text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{Cl}^- + \text{HClO} \\
\text{HClO} & \rightarrow \text{H}^+ + \text{ClO}^- 
\end{align*}
\]

Firstly, the electrode exchanged electrons with water to generate hydroxyl radicals (MO$_x$(·OH)) as adsorbent, which reacted with chloride ions to produce hypochlorite active group (MO$_x$(·OCl)) and chlorine gas, or chloride ions directly exchanged electrons with the electrode to produce chlorine gas. This process is shown in Equations (1)–(5). Thereafter, the generated chlorine gas reacted with water to produce hypochlorous acid. MO$_x$(·OH), MO$_x$(·OCl), chlorine gas, and hypochlorous acid were used to indirectly oxidize ammonia-nitrogen, as shown in Equations (6) and (7). In the present study, the Pd-Sn modiﬁed Ru-Ir electrode in saturated sodium chloride solution exhibited good performance of both chlorine-evolution and electrical conductivity, which was conducive to the progress of the chlorine-evolution reaction and promoted the generation of the residual chlorine. Therefore, it can be concluded that the modified Ru-Ir electrode with Pd-Sn was suitable for the application of electro-catalytic oxidation of ammonia-nitrogen with chloride ions as the medium.

3.2. Effect of reaction conditions on electro-catalytic oxidation of ammonia-nitrogen
3.2.1. Effect of chloride ion concentration
Figure 2(a) illustrates the influence of chloride ion concentration on ammonia-nitrogen removal at the initial ammonia-nitrogen concentration of 50 mg/L. As shown in Figure 2(a), compared to low chloride concentration, high ammonia-nitrogen removal rate could be achieved with high concentration of chloride ion at...
the same reaction time, indicating that the high level of chloride ion was conducive to promoting the electro-catalytic removal of ammonia-nitrogen. For instance, the removal rates of ammonia-nitrogen at the reaction time of 30 min were 8.70%, 12.13%, 39.73%, 66.84%, and 97.91%, respectively, when the chloride ion concentrations were 1000, 3000, 5000, 7000 mg/L and 10,000 mg/L, respectively. However, the increase of the chloride ion concentration exerted different influences on the removal rate of ammonia-nitrogen. As the concentration of chloride ions increased from 1000 to 3000 mg/L, the removal rate of ammonia-nitrogen increased by 1.72% for each 1000 mg/L increase of chloride ion concentration. When the concentration of chloride ion was in the range of 3000–5000 mg/L, the removal rate of ammonia-nitrogen increased by 13.8% for every 1000 mg/L increase in chloride ion concentration. What is more, the concentration of chloride ion ranged from 5000 to 7000 mg/L, and the removal rate of ammonia-nitrogen increased by 13.56% for each 1000 mg/L increase of chloride ion concentration. However, the concentration of chloride ion was in the range of 7000–10,000 mg/L, and the removal rate of ammonia-nitrogen increased by 10.35% for every 1000 mg/L increase of chloride ion concentration. This finding indicated that with the increase of chloride ion concentration, the effective removal rate of ammonia-nitrogen by chloride ion increased firstly and then decreased. It was evidenced that the optimal chloride ion concentration should be maintained at 5000–7000 mg/L to keep the high efficiency of removal rate of ammonia-nitrogen.

To achieve the same ammonia-nitrogen removal rate of 25.78%, the time required for ammonia-nitrogen removal were 90.00, 60.00, 18.52, 11.19, and 7.75 min, as the chloride ion concentrations were 1000, 3000, 5000, 7000, and 10,000 mg/L, respectively. The higher the concentration of chloride ions, the shorter the electro-catalytic time needed for ammonia-nitrogen removal. When the concentration of chloride ions was less than 5000 mg/L, the required time was approximately 60 min, while the concentration of chloride ions was greater than 5000 mg/L, the required time was about 20 min. This finding implied that the optimal concentration of chloride ion should be kept at least 5000 mg/L. In summary, in the process of electro-catalytic oxidation treatment of the high chlorine ammonia-nitrogen wastewater, the chloride ion concentration should be kept around 5000–7000 mg/L. Excessive chloride ion concentration would reduce the efficiency of ammonia-nitrogen removal, increase the cost of reagents, and affect the subsequent treatment of wastewater. Therefore, it is necessary to comprehensively consider the concentration of chloride ions concentration for ensuring the effective removal of ammonia-nitrogen in the actual process of electro-catalytic treatment for the high chlorine ammonia-nitrogen. In the present study, the chloride ion concentration of 5000 mg/L was selected for subsequent experiments.

3.2.2. Effect of pH

Figure 2(b) shows the influence of pH on the removal rate of ammonia-nitrogen when the initial concentration of ammonia-nitrogen was 50 mg/L, with the concentration of chloride ions of 5000 mg/L. As the reaction time was short, pH exhibited little effect on the removal of ammonia-nitrogen. When the electro-catalytic reaction time exceeded 40 min, the removal efficiency of ammonia-nitrogen increased with the increase of initial pH. The removal rates of ammonia-nitrogen at the reaction time of 50 min were 46.46%, 54.52%, 55.97%, 69.45%, and 72.27% at the pH was 3, 5, 7, 9, and 11, respectively. The experimental results revealed that with the increase of pH, the removal rate of ammonia-nitrogen gradually increased, suggesting that alkaline conditions were more conducive to the
electro-catalytic oxidation of ammonia-nitrogen. The reason behind this phenomenon might be that there was a large amount of hydroxide (OH\(^-\)) in the solution under alkaline conditions, and chlorine gas was more likely to transform into oxidizing substances, such as sodium hypochlorite, which promoted the removal of ammonia-nitrogen. In addition, since a large amount of H\(^+\) existed in the acidic solution, the ionic radius of ammonia-nitrogen. In addition, since a large amount likely to transform into oxidizing substances, such as under alkaline conditions, and chlorine gas was more directly volatilized from the wastewater. Thus, few oxidizing substances, such as hypochlorous acid produced in the solution, were observed, resulting in the poor removal of ammonia-nitrogen. By comparison, it was found that when the initial pH was 9 and 11, the difference in the removal rate of ammonia-nitrogen was small (2.82%), suggesting that the increase in the initial pH of the ammonia-nitrogen wastewater had a small promoting effect on the ammonia-nitrogen removal. If the initial pH was too high, a large amount of alkali needs to be added, which would increase the reagent cost. Therefore, the effective removal of ammonia-nitrogen can be promoted by controlling the initial pH of ammonia-nitrogen wastewater in the process of electro-catalytic treatment of ammonia-nitrogen wastewater.

3.2.3. Effect of temperature

Figure 2(c) depicts the influence of reaction temperature on the removal of ammonia-nitrogen at the initial concentrations of ammonia-nitrogen and the concentration of chloride ion of 50 and 5000 mg/L, respectively. Reaction temperature directly affected the energy of the reactions and the migration rate of pollutants between the bulk solution and the electrode surface [47], leading to the variety in removal efficiency of pollutants. The temperature could significantly affect the removal effect of ammonia-nitrogen. When the temperature was 30°C, 40°C, 50°C, 67°C, and 78°C, respectively. As the temperature was between 30°C and 40°C, the difference of the slope of the fitting line of the ammonia-nitrogen removal curve was 0.93, 1.00, 1.32, 1.58, and 1.92, respectively, indicating a positive correlation between the temperature and the ammonia-nitrogen removal rate. As the temperature was between 30°C and 40°C, the difference of the slope of the ammonia-nitrogen removal curve was only 0.07, indicating that temperature played a minor role in ammonia-nitrogen removal when the temperature was less than 40°C. When the temperature was greater than 40°C, the larger slope of the ammonia-nitrogen removal curve was observed with the increase in temperature, suggesting that the ammonia-nitrogen removal rate increased rapidly. At a reaction time of 50 min, the removal efficiencies of ammonia-nitrogen were 46.74%, 48.50%, 66.67%, 76.90%, and 93.01%, at temperature of 30°C, 40°C, 50°C, 67°C, and 78°C, respectively. To ensure that the removal efficiency of ammonia-nitrogen (≥66.67%) was high, the electro-catalytic treatment temperature should be greater than 50°C. The influence of temperature on ammonia-nitrogen removal was mainly through increasing the energy of the system to improve the reaction rate of the system and then reducing the resistance of ammonia-nitrogen removal. In addition, the Brownian motion of the molecules in the system was intensified with the increase of temperature, which improved the contact opportunity between the ammonia-nitrogen molecules, and promoted the electro-catalytic removal of ammonia-nitrogen. In summary, the electro-catalytic oxidation of ammonia-nitrogen removal rate can be improved by regulating the reaction temperature (≥40°C), however, the high temperature would increase energy consumption. Therefore, it is necessary to take an overall consideration on the energy consumption, the service life of the equipment, and the removal efficiency of ammonia-nitrogen to rationally adjust and control the reaction temperature of electro-catalytic treatment of ammonia-nitrogen.

3.3. Kinetic studies

Figure 3(a, c, and e) presents the influence of chloride ion concentration, pH, and temperature on the removal effect of ammonia-nitrogen. It can be seen that the electro-catalytic removal process of ammonia-nitrogen belonged to the zero-order reaction, since there was a linear relationship between the residual ratio of ammonia-nitrogen and the reaction time under different reaction conditions. The reaction rates, half-lives (t\(_{1/2}\)), and linear correlation coefficients under different conditions are shown in Table 1. The relationship between different reaction conditions and reaction rates is shown in Figure 3(b, d, and f).

Combined with the analysis in Table 1 and Figure 3(b, d, and f), it can be found that the higher the concentration of chloride ions, the faster the removal reaction rate of ammonia-nitrogen, indicating that the concentration of chloride ions could promote the reaction rate of ammonia-nitrogen removal. The reaction rate of the electro-catalytic processes increased with the increase of pH and temperature, respectively. The reaction rate of the electro-catalytic processes was positively correlated with chloride ion concentration(8), pH(9) and temperature(10), respectively, as below:

\[ y = 3.5148 \times 10^{-6} x - 0.0036 \quad \left( R^2 = 0.9650 \right) \]  

(8)
where \( y \) denotes the reaction rate of ammonia-nitrogen removal (\( \text{min}^{-1} \)) and \( x \) denotes the concentration of chloride ion (mg/L).

\[
y = 7.0000 \times 10^{-4}x + 0.0075 \quad (R^2 = 0.9615)
\]  

where \( y \) represents the reaction rate of the electro-catalytic processes (\( \text{min}^{-1} \)) and \( x \) represents pH.

\[
y = 2.0792 \times 10^{-4}x + 0.0025 \quad (R^2 = 0.9873)
\]  

where \( y \) denotes the reaction rate of ammonia-nitrogen removal (\( \text{min}^{-1} \)) and \( x \) denotes the temperature (°C).

According to Equation (8), taking the reagent cost and wastewater post-treatment into consideration,
high chloride ion concentrations would increase the cost of the wastewater treatment and cause pressure on subsequent treatment facilities. Therefore, in the process of electro-catalytic treatment of high chlorine ammonia-nitrogen wastewater, the concentration of chloride ion should be controlled at 5000–7000 mg/L to achieve both cost-effectiveness and high removal efficiency of ammonia-nitrogen. From Equation (9), it can be seen that the pH in the wastewater should be greater than 7 to achieve the effective and rapid electro-catalytic removal of ammonia-nitrogen. Equation (10) illustrates high temperature should be selected to achieve the effective and rapid removal of ammonia-nitrogen in the electro-catalytic process. However, given the fact that high temperature would cause high energy consumption and accelerate the corrosion damage of equipment, the reaction temperature should be maintained at 50°C.

### 3.4. The apparent activation energy

The reaction rates of the electro-catalytic process at 30°C, 40°C, 50°C, 67°C, and 78°C are shown in Table 2. The apparent activation energy in the electro-catalytic process was calculated using the Arrhenius equation, as below:

\[
\ln k = -\frac{E_a}{RT} + \ln A
\]  

(11)

where \( E_a \) denotes activation energy, kJ/mol; \( R \) denotes the gas molar constant, 8.314 J/(mol·K); \( K \) denotes the removal rate of ammonia-nitrogen, min\(^{-1}\); \( A \) denotes the pre-exponential factor, min\(^{-1}\); and \( T \) denotes the thermodynamic temperature, K.

According to the data in Table 2, the \( \ln k \sim \frac{1}{T} \) diagram can be got as in Figure 4. And formula (12) was obtained by fitting curve with origin software:

\[
\ln(k) = -1694.58 \times \frac{1}{T} = 0.8595 \quad (R^2 = 0.9865)
\]  

(12)

The high correlation coefficient \( (R^2 > 0.98) \) of the fitting curve indicated a high accuracy. According to formula (12), when \(-\frac{E_a}{R}\) was \(-1694.58\), \( E_a \) was equal to 14.089 kJ/mol, and the apparent activation energy was 14.089 kJ/mol accordingly. This finding suggested that higher temperature could enhance the removal rate of ammonia-nitrogen.

### 3.5. The possible denitrification pathway for ammonia-nitrogen removal

#### 3.5.1. Electrode surface reaction process

Figure 5(a) describes the CV curves of high chlorine ammonia-nitrogen wastewater. It can be seen that the curves were similar at different scanning speeds, with only one redox peak. When the voltage was approximately 1.05 V, the current increased rapidly. This finding might be attributed to the generation of chlorine gas. The chloride ions diffused to the electrode surface were converted into chlorine gas, and the ammonia-nitrogen can be indirectly oxidized and removed by the chlorine gas in the electro-catalytic processes.

Figure 5(b) illustrates the Nyquist plot of the Pd-Sn modified Ru-Ir electrode at concentrations of 5000 mg/L chloride ion and 80 mg/L ammonia-nitrogen. \( Z' \) denotes the real part and \( Z'' \) denotes the imaginary part.
Section a–b was arc-shaped, presenting the stage of charge transfer control. After b, the curve changed differently with the increase of voltage. When the voltage was 1.1 V, the mixture control of charge transfer and diffusion occurred between sections b and c, and the straight line slope (near 45°) after Section c indicated the stage of diffusion control. As the voltage increased to 1.2 V, the slope between b and d was a straight line with a slope less than 45°, implying the stage of diffusion control in terms of barrier layer. After Section d, the curve presented an arc shape, suggesting the stage of charge transfer control. When the voltage was 1.15 V, Section b presented a straight line with the slope less than 45°, suggesting the stage of diffusion control subject to the barrier layer. Moreover, the voltage of 1.15 V seemed to be the critical conversion point between charge transfer control and diffusion control. In summary, there was a diffusion barrier layer between the electrode and the solution during the treatment of high chlorine ammonia-nitrogen wastewater. The barrier layer increased the contact resistance between chloride ions and the electrode surface, which was one of the limiting factors for the treatment of high chlorine ammonia-nitrogen wastewater. Therefore, it is necessary to control the electrode voltage to be greater than 1.15 V to break through the limitation of diffusion barrier layer, leading to the enhanced removal of ammonia-nitrogen.

### 3.5.2. Properties of electrolytes

Figure 6 presents the effect of electrolyte on ammonia-nitrogen removal at the initial ammonia-nitrogen concentration of 80 mg/L. It can be seen that higher removal efficiency of ammonia-nitrogen was observed when sodium chloride was used as the electrolyte, compared to sodium sulfate. Furthermore, the ammonia-nitrogen removal rate of 100% was observed when the electro-catalytic reaction time was 40 min at a chloride ion concentration of 5000 mg/L. By contrast, the removal rate of ammonia-nitrogen was only 13.19% at the concentration of sodium sulfate of 10,000 mg/L. This finding indicated that the contribution of indirect electro-catalytic processes played an essential role in ammonia-nitrogen oxidation, accounting for 86.81% of the total ammonia-nitrogen removal. The chloride ions was first converted into chlorine gas by the electrode, and then the ammonia-nitrogen was oxidized and...
removed by chlorine gas in the high chlorine ammonia-nitrogen wastewater. In the chlorine-free ammonia-nitrogen solution, ammonia-nitrogen was oxidized by directly contacting with the electrode or reacting with hydroxyl radicals on the electrode surface. In this process, a large number of oxygen evolution as side reactions occurred on the electrode surface, producing a large number of bubbles, which prevented the direct contact between ammonia-nitrogen and the electrode. Thus, the presence of hydroxyl radicals was short, resulting in extremely low ammonia-nitrogen removal without chlorine. In summary, indirect oxidation was the main process in the electro-catalytic oxidation for treating the high chlorine ammonia-nitrogen wastewater, and the chloride ion acted as the ‘oxidant’ for the removal of ammonia-nitrogen.

**3.5.3. The reactants in ammonia-nitrogen removal**

Figure 7(a) depicts the changes in the content of NO$_3$-N, NO$_2$-N, and TN. The initial concentrations of ammonia-nitrogen, TN, and chloride ion were 80, 80, and 5000 mg/L, respectively. Because only ammonia-nitrogen existed in the original high chlorine ammonia-nitrogen wastewater, the concentrations of nitrite and nitrite at reaction time of 50 min were 2.11 and 1.89 mg/L, respectively, as the oxidation products of ammonia-nitrogen. At the same time, the removal rate of TN was increasing, and the removal rate of TN reached 95.01% at 50 min, indicating that nitrogen was nearly completely removed from the solution. Therefore, it can be inferred that nitrogen-containing substances in the wastewater were transformed into nitrogen and separated from the water. To sum up, the products of ammonia-nitrogen removal by electro-catalytic oxidation was nitrogen, in addition to a small amount of NO$_3$-N and NO$_2$-N.

Figure 7(b) illustrates the schematic diagram of hydroxyl radical production at the initial ammonia-nitrogen and chloride ion concentrations of 80 and 5000 mg/L. It was evidenced that hydroxyl radicals

![Figure 7](image_url)

**Figure 7.** The reactants at the initial ammonia-nitrogen and chloride ion concentrations of 80 and 5000 mg/L: (a) the amount of NO$_3$-N, NO$_2$-N, and TN and (b) the hydroxyl radical production.

![Figure 8](image_url)

**Figure 8.** Denitrification process of electro-catalytic oxidation of ammonia-nitrogen.
were generated in the process of ammonia-nitrogen removal. As shown in Figure 7(b), the content of hydroxyl free radical increased significantly after 30 min, however, the content was very low. The contribution of hydroxyl radicals to ammonia-nitrogen removal was trivial, due to the extremely low hydroxyl radicals content.

3.5.4. Denitrification process

The analysis of the intermediate products in the process of electro-catalytic oxidation for treating ammonia-nitrogen wastewater elucidated that under the action of the ‘oxidant’ chloride ion, ammonia-nitrogen was eventually converted to nitrogen. Although the hydroxyl radical oxidation process may have existed in the denitrification process, the contribution of free radical oxidation was minor. The specific denitrification process is shown in Figure 8.

4. Conclusions

This study investigated the performance of the modified Ru-Ir electrode with Pd-Sn for treating high chlorine ammonia-nitrogen wastewater. The effects of reaction conditions on the removal of ammonia-nitrogen, kinetics, and possible denitrification process were also clarified. The main conclusions are as follows:

1. The chlorine-evolution potential of the Pd-Sn modified Ru-Ir electrode was 1.0956 V (vs. SCE), which was much lower than that of the commercial Ru-Ir electrode (1.1663 V vs. SCE).
2. The Pd-Sn modified Ru-Ir electrode can efficiently treat the high chlorine ammonia-nitrogen wastewater. With the initial ammonia-nitrogen and chloride ion concentrations of 80 and 5000 mg/L, as well as current of 0.5 A, the removal efficiency of ammonia-nitrogen could reach 100% at the reaction time of 40 min.
3. The rule of treating ammonia-nitrogen using electro-catalytic oxidation technology conformed to the zero-order kinetic law, and the removal process was the endothermic reaction with the apparent activation energy of 14.089 kJ/mol.
4. Indirect oxidation played a vital role in the electro-catalytic denitrification of ammonia-nitrogen. With the ‘oxidant’ chloride ion, ammonia-nitrogen was eventually converted to nitrogen. And the hydroxyl radicals made little contribution to oxidation denitrification in the electro-catalytic process.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Data availability statement

Data available on request from the authors. The data that support the findings of this study are available from the corresponding author [WY Xie] upon reasonable request.

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