

Unravelling the Electro-Catalytic Treatment of Acrylonitrile Wastewater using the Mn/Sn Doping Ru-Ir Electrode: Kinetics, Optimization and Mechanism

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Abstract

The prepared Mn/Sn doping Ru-Ir electrode was used as the anode to investigate the removal of acrylonitrile wastewater by electro-catalytic technology. The oxygen evolution potential and chlorine evolution potential of Mn/Sn doping Ru-Ir electrode were 1.3278V (vs. SCE) and 1.1243V (vs. SCE), respectively, which were better than those of Ru-Ir electrode. The kinetics of electro-catalytic treatment of acrylonitrile accorded with the zero-order kinetics equation. Response surface Methodology (RSM) explained that the interaction of voltage, current and pH on the removal rate of acrylonitrile was consistent with the 2FI model. What's more, the optimal treatment conditions were as follows: pH was 10.12, reaction time was 39.64 min, and current was 0.81 A. The electro-catalytic removal of acrylonitrile was mainly dominated by direct oxidation coupled with indirect oxidation. Acrylonitrile gained and lose electrons on the electrode surface to be directly degraded, and was also directly oxidized by hydroxyl radicals adsorbed on the electrode surface (OHads). In addition, free chlorine and hydroxyl free radicals (OH free) desorbed from the electrode surface can indirectly mineralize acrylonitrile. The removal rate of acrylonitrile, the denitrification rate, and the mineralization rate of organic matter could reach 100.00%, 85.87%, and 72.40%, respectively. In the light of experimental results, Mn/Sn doping Ru-Ir electrode would be a promising anode for acrylonitrile removal, and the electro-catalytic technology was confirmed to be efficient to treat acrylonitrile wastewater with the effect of denitrification and organic mineralization.

Keywords: Mn/Sn doping Ru-Ir electrode; Acrylonitrile; 2FI model; Direct oxidation coupled with indirect oxidation; The electro-catalytic technology

Introduction

Acrylonitrile is an crucial industrial raw material, which is widely used in synthetic plastics, acrylic fiber, and synthetic rubber. More than 5 million tons of acrylonitrile each year, accompanying with equal amount of wastewater [1]. Acrylonitrile in wastewater is one of the 129 priority toxic chemicals specified by the U.S. Environmental Protection Agency (EPA), and its content ranges from 50 mg/L to 2000 mg/L [2]. The wastewater containing the acrylonitrile is highly toxic and difficult to be biochemically treated. Once acrylonitrile wastewater enters the water environment, it will seriously damage the water ecosystem and threaten the human health.

Conventional physical and chemical treatments such as adsorption method, biochemical method and Advanced Oxidation Processes (AOPs) have been intensively employed for removal of acrylonitrile [2-10]. However, limitations exist for application these methods. For example, adsorption has been employed as the efficient method to removal acrylonitrile. Nonetheless, the acrylonitrile only experiences physical transfer from aqueous phase to the absorbent without being destructed. Additionally,

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desorption of acrylonitrile from the absorbent is time-consuming. Pretreatment for diluting the concentrations of the acrylonitrile is required prior to utilizing biochemical method, since high concentration of acrylonitrile hinders the biochemical treatment efficiency. Supercritical water oxidation, photo catalysis, and Fenton-like catalysis are typical methods for efficient destruction of acrylonitrile, yet they suffer from drawbacks such as strict reaction conditions, high energy consumption and easily produced secondary pollution.

Electrocatalysis has been emerging as a potent wastewater treatment method with the merits such as, high efficiency, no secondary pollution, strong operability, and low requirements of reaction conditions [11, 12]. The key of electrocatalysis for aqueous organic-contaminants elimination is electrode materials. PbO_2 , $\text{PbO}_2\text{-CeO}_2$, $\text{Ti/SnO}_2\text{-Sb}$, $\text{Pt/Ru-Ti/SnO}_2\text{-Sb}$, and $\text{Ti/SnO}_2\text{-RuO}_2$ have been widely used as electrode materials, yet low degradation efficiency and poor electrode stability become the bottlenecks for their further application. For a long time, the Ru-Ir electrode has been studied in medical detection energy-conversion, oxygen evolution, chlorine evolution, and environmental remediation because of its good electrochemical performance and stability [13-25]. However, the Ru-Ir electrode has the problems of low hydroxyl radical yield and low organic removal rate in the process of electrocatalytic treatment of organic wastewater. To solve these problems, the Mn/Sn doping Ru-Ir electrode has been prepared by combining the advantages of Mn and Sn oxide electrodes by our research group, and the overall electrochemical performance has been fundamentally improved [26]. However, the detailed electrocatalytic effects of the Mn/Sn doping Ru-Ir electrodes and the mechanistic insight into the organic destruction still remain to be unveiled (**FIG. 1**).

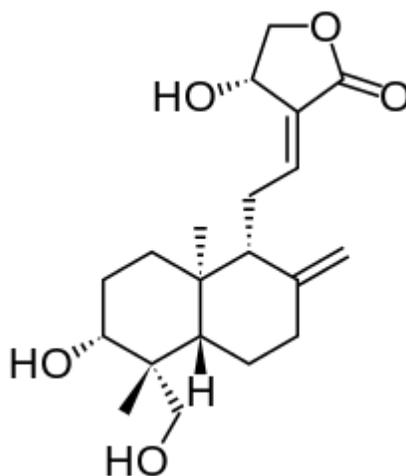


FIG. 1. Chemical structure of andrographolide.

In this work, the Mn/Sn doping Ru-Ir electrode is used to discuss the kinetics and mechanism of electro-catalytic treatment of acrylonitrile simulated wastewater. More specifically, this research is aimed to:

1. evaluate the electrochemical performance of the Mn/Sn doping Ru-Ir electrode;
2. investigate the influence rules of reaction conditions on electro-catalytic treatment of acrylonitrile;
3. optimize multi-factor treatment conditions of simulated acrylonitrile wastewater using Response Surface Methodology (RSM);
4. explore the possible process products and reaction mechanism of electro-catalytic treatment of acrylonitrile.

Experimental Methods

Experimental setup

Electrocatalytic reaction unit was a customized electrolytic cell with an effective volume of 200 mL. The Mn/Sn doping Ru-Ir electrode (5.4 cm×5.0 cm×0.2 cm) and the platinum electrode (5.4 cm×5.0 cm×0.2 cm) was used as the anode and the cathode, respectively. The anode and cathode were separated by 4 cm and parallel in the electrocatalytic reaction unit. The rotating speed of the magnetic stirrer was set at 700 rpm. The electrocatalytic current and voltage were provided by a DC Power Supply (DH1718E-5 DC Power Supply, Beijing Dahua Radio Instrument Factory, and China). The initial pH was adjusted by Hydrochloric acid (HCl) and Sodium Hydroxide (NaOH). All the experimental parameters were kept the same for different experiments. During the experiment, wastewater samples were taken every 10 min to detect water sample indexes, including the concentration of acrylonitrile, Ammonia-Nitrogen ($\text{NH}_3\text{-N}$), Nitrite-Nitrogen ($\text{NO}_2\text{-N}$), Nitrate-Nitrogen ($\text{NO}_3\text{-N}$), Total Nitrogen (TN), residual chlorine and Total Organic Carbon (TOC).

Preparation of the acrylonitrile simulated wastewater

8.2394 g sodium chloride and 1.25 mL acrylonitrile stock solution were added into a 500 mL beaker with a proper amount of ultra-pure water. And then the solution in the beaker, together with the solution of rinsing the beaker and glass rod for three times, are transferred into a 1000 mL volumetric flask, after that, the volumetric flask was filled with ultra-pure water to 1000 mL. Finally, the volumetric flask was shaken well to obtain well-mixed acrylonitrile simulated wastewater. The resulted solution contained 5000 mg/L chloride ion and 1000 mg/L (or 18.85 mol/L) acrylonitrile, TN was 264.15 mg/L, TOC was 680.00 mg/L, and the concentration of $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, free chlorine and total chlorine were all zero.

RSM experimental design

In order to understand the potential relationship between predicted variables (independent variables) and response variables (dependent variables) and calculate the approximate value of functional response of corresponding independent variables, the comprehensive influence of process parameters or independent variables on each response value is studied by using Design Expert 10 software through experimental design, mathematical modeling and process optimization with the principle of response surface methodology [27]. On the basis of single factor test results, the current, reaction time, and initial pH (represented by x_1 , x_2 , and x_3 , respectively) were taken as independent variables, and acrylonitrile removal rate (Y) was taken as dependent variable. According to the design principle of Box-Behnken Design (BBD), the minimum value, median value, and maximum value of each related parameter are determined. **TABLE 1** shows the independent variable parameters and their levels in this study. With the help of the Design Expert 10 software, the specific experimental parameters of response surface model are designed, and the experimental results are processed and analyzed.

TABLE 1. The parameters and levels of RSM independent variables.

Factors		Unit	Level		
x_1	Current	A	0.5	0.75	1
x_2	Reaction time	min	30	40	50
x_3	pH	—	7	9	11

The 2FI response model can describe the system behavior and predict the relationship between independent variables and response variables, which can be expressed by polynomial equation, as shown in equation (1)

$$y = a_0 + \sum_{i=1}^n a_i x_i + \sum_{i < k}^n a_{ik} x_i x_k + \varepsilon_0 \quad (1)$$

where, y represents response value or dependent variable (acrylonitrile removal rate), x_i and x_k are independent variables or factors, a_0 represents constant coefficient or intercept constant, and a_i and a_{ik} are linear coefficient and interaction coefficient respectively. N is the number of study factors, and ε_0 is the error.

The test of statistical significance must be based on the total error standard with the confidence level of 95.0% ($p < 0.05$). R_2 ranges from 0 to 1, and R_2 is used to express the fitting properties of polynomial model equations. When R_2 value is closer to 1, the model is more accurate. In order to study the interactive influence of process variables on response, a three-dimensional response surface graph is established.

Analytical methods for electrochemical performance

The electrochemical workstation (CHI660E Shanghai Chenhua Instrument Co., Ltd.) was used to detect the electrochemical performance of the Mn/Sn doping Ru-Ir electrode. and the Saturated Calomel Electrode (SCE), platinum electrode, and the Mn/Sn doping Ru-Ir electrode were used as the reference electrode, the auxiliary electrode, and working electrode, respectively. In order to obtain the oxygen evolution potential and chlorine evolution potential, the linear voltammetry curves (LSV) of the Mn/Sn doping Ru-Ir electrode were measured in saturated sodium chloride solution (NaCl) and 0.5 mol/L sulfuric acid (H_2SO_4), respectively. The Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) of the Mn/Sn doping Ru-Ir electrode were determined in the acrylonitrile simulated wastewater. And the acrylonitrile removal rate was calculated by formula (1) [26].

Methods for testing water quality indicators

A pH meter was used to measure the pH. $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ were measured using a gas phase molecular absorption spectrometer (GMA3378, China), and TOC and TN were determined by a liquid phase total organic carbon analyzer (TOC-VCPH, Japan). The free chlorine and total chlorine were determined by DPD reagent (HJ 586-2010), and the bound chlorine was the difference between total chlorine and free chlorine. The gas chromatography-mass spectrometry (GC-MS, USA) was used to determine the concentration of acrylonitrile and its reaction products [26]. High Performance Liquid Chromatography (HPLC, USA) measured the sum of 2,3-dihydroxybenzoic acid and 2,5-dihydroxybenzoic acid content to determine the concentration of hydroxyl radical. HPLC included LC-10AT vacuum degassing pump, DGU-12A quaternary pump, SIL-10AD autosampler, Japan Shimadzu RF-10AXL fluorescence detector, etc. The chromatographic column was XDB-C18 column ($5\ \mu\text{m}\times 4.6\ \text{mm}\times 150\ \text{mm}$), mobile phase was 3% acetic acid solution-Methanol (75:25) at the flow rate of 1.0 mL/min, the injection volume was 10 μL , column temperature was 30°C, and retention time was 25 min. All water used was secondary deionized water.

Results and Discussions

The electrochemical performance

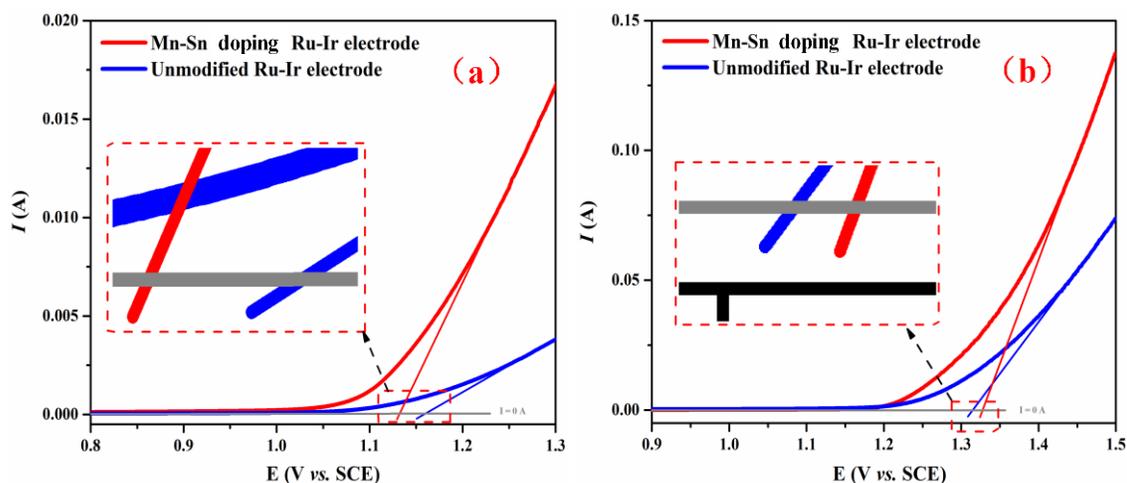


FIG. 2. Linear scan voltammogram curves, (a) the chlorine evolution potential in saturated sodium chloride solution, (b) the oxygen evolution potential in 0.5 mol/L H_2SO_4 solution.

FIG. 2a displayed the chlorine evolution potential between Ru-Ir electrode and the Mn/Sn doping Ru-Ir electrode (vs. SCE) at a scanning rate of 5 mV/s. In order to investigate the effect of Mn-Sn modified on the chlorine evolution performance of Ru-Ir electrode, the chlorine evolution potentials of the electrode were measured and can be obtained at the intersection of the tangent and the horizontal axis of the straight line segment of the curve [28]. The chlorine evolution potential of the Ru-Ir electrode and the Mn/Sn doping Ru-Ir electrode were 1.1663 V and 1.1243 V (vs. SCE) respectively. The chlorine evolution potential of the Mn/Sn doping Ru-Ir electrode was lower, indicating that the Mn/Sn doping Ru-Ir electrode had a better chlorine evolution performance. At 1.3 V, the current of the Ru-Ir electrode and the Mn/Sn doping Ru-Ir electrode were 0.0040 A and 0.0170 A, respectively, declaring that the conductivity of the Mn/Sn doping Ru-Ir electrode was better than that of the Ru-Ir electrode. Therefore, this phenomenon suggested that the Ru-Ir electrode material with co-doping of Mn and Sn could maintained the lower the chlorine evolution potential, promoting the utilization rate of current in saturated sodium chloride solution, which was conducive to the chlorine evolution reaction.

FIG. 2b illustrated the oxygen evolution potential between the Ru-Ir electrode and the Mn/Sn doping Ru-Ir electrode (vs. SCE) at a scanning rate of 5 mV/s. The oxygen evolution potentials were measured for exploring the effect of Mn-Sn modified on the chlorine evolution performance of Ru-Ir electrode, and obtained at the intersection of the tangent and the horizontal axis of the straight line segment of the curve [28]. The oxygen evolution potential of the Ru-Ir electrode and the Mn/Sn doping Ru-Ir electrode were 1.3145 V and 1.3278 V (vs. SCE), respectively. The oxygen evolution potential of the Mn/Sn doping Ru-Ir electrode was the higher. At 1.5 V, the current of the Ru-Ir electrode and the Mn/Sn doping Ru-Ir electrode were 0.0735 and 0.1371 A, respectively, indicating that the conductivity of the Mn/Sn doping Ru-Ir electrode had better conductivity than that of the Ru-Ir electrode in 0.5 mol/L H_2SO_4 solution [26]. What's more, the Mn/Sn doping Ru-Ir electrode with higher oxygen evolution potential can better inhibit oxygen evolution, promoting the generation of hydroxyl radicals, active

active oxygen and other active groups, because the following oxygen generation process existed on the electrode surface [29].



When the oxygen evolution potential increased, the resistance caused by oxygen generation in reaction (4), increased, and the content of MO_{x+1} increased which inhibited the progress of reaction (3) and promoted the accumulation of hydroxyl radical and reactive oxygen species. The high concentration of hydroxyl radical and reactive oxygen species can accelerate the degradation of acrylonitrile.

The yield of hydroxyl radical

FIG. 3 described the hydroxyl radical production of the Ru-Ir electrode and the Mn/Sn doping Ru-Ir electrode in 200 mL of 10 g/L sodium sulfate solution. The hydroxyl radical production were measured to investigate the effect of the co-doping of Mn-Sn in Ru-Ir electrode on the hydroxyl radical production. The Mn/Sn doping Ru-Ir electrode yielded the most hydroxyl radicals than that of the Ru-Ir electrode at any same reaction time. When the reaction time was 50 min, the hydroxyl radical yields of the Ru-Ir electrode and the Mn/Sn doping Ru-Ir electrode were 0.9370 mmol/L and 1.2044 mmol/L, respectively. Combined with **FIG.2b**, it can be declared that co-doping of Mn-Sn on the Ru-Ir electrode improved the oxygen evolution potential, promoting the yields of the hydroxyl radicals, and there was a positive proportional increase relationship between the oxygen evolution potential and the production of hydroxyl radicals. Hence, the Mn/Sn doping Ru-Ir electrode with higher oxygen evolution potential, was more conducive to treat the acrylonitrile simulated wastewater.

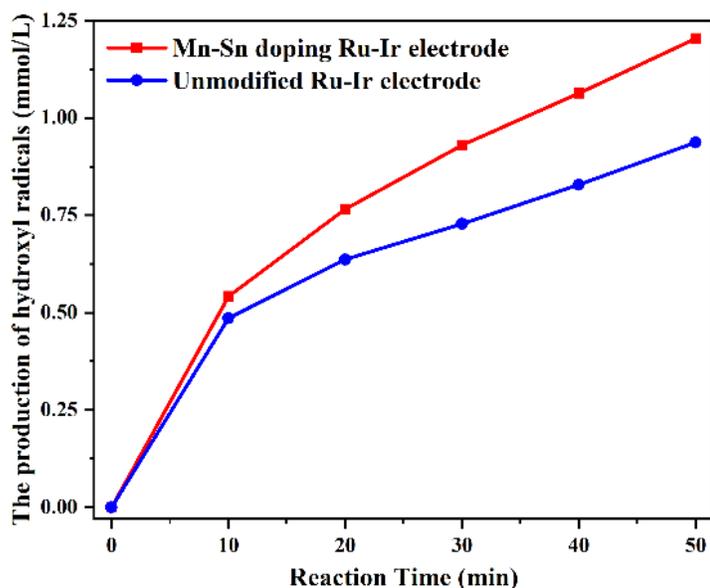


FIG. 3. The hydroxyl radical production of the Ru-Ir electrode and Mn/Sn doping Ru-Ir electrode.

Effect of reaction conditions on acrylonitrile removal rate

Electrocatalytic advanced oxidation method can effectively remove acrylonitrile, and depends on a variety of reaction conditions, such as pH, voltage and current. However, the electrocatalytic reactions are complicated and not entirely clear.

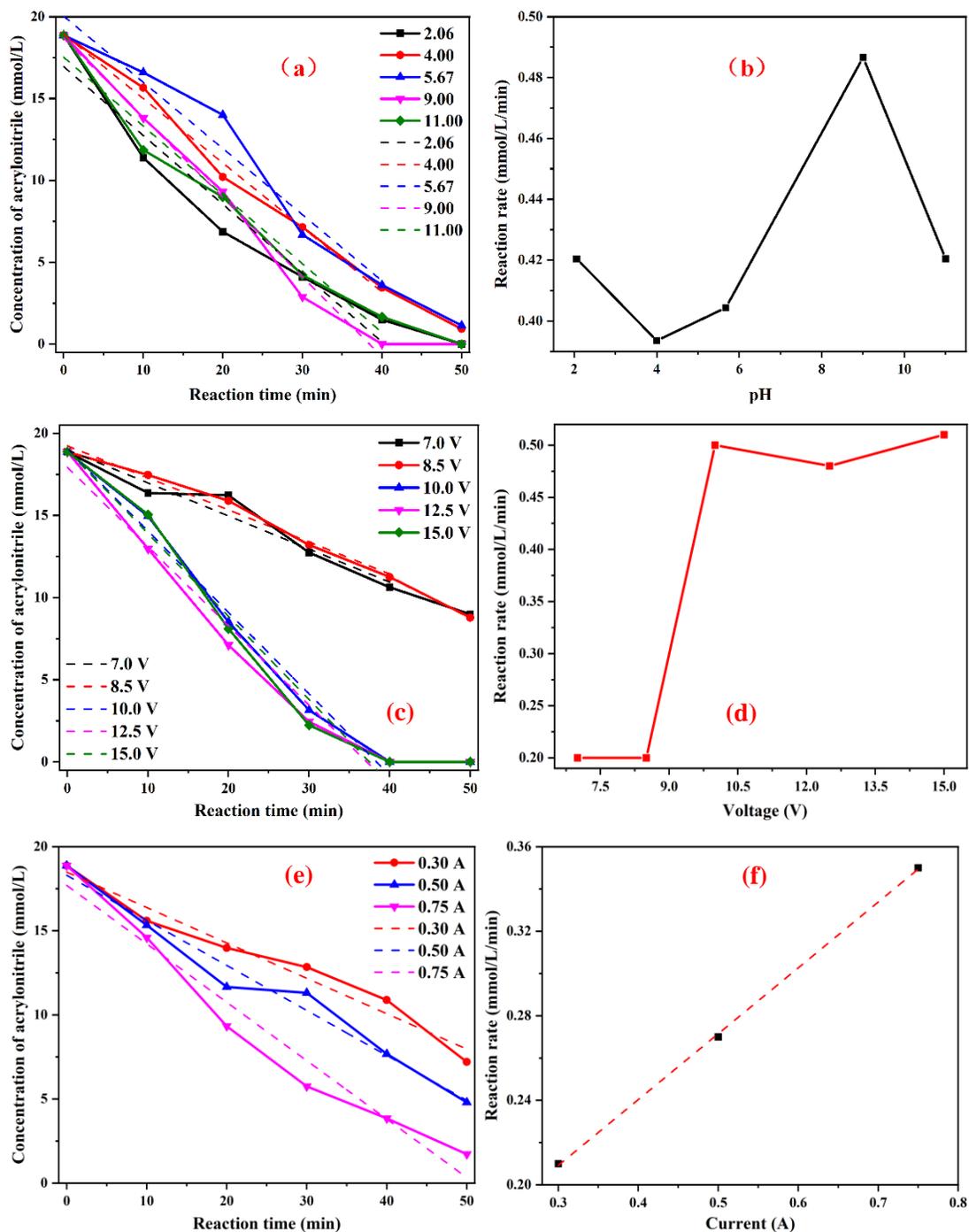


FIG. 4. Influence of initial pH(a), voltage(c) and current(e) on acrylonitrile removal (dotted line is the fitting regression line relationship), and Relationship between pH(b), voltage(d), current(f) and reaction rate, respectively.

The effect of pH

Especially in the process of indirect electro-oxidation, the pH of electrolytic medium controlled the ratio of H^+/OH^- , and affected the formation and activity of intermediate active substances (such as Cl_2 , $HClO$, ClO^- , Cl^- , OH^- , HO_2^- and O_2^- , etc.), so pH was considered as an important parameter of electrochemical system. In this case, NaCl was the electrolytic medium, and NaOH and H_2SO_4 were used for pH adjustment. In the chlorine-rich medium, Cl_2 , $HClO$ and ClO^- , as the main intermediate active chlorine (oxidation) substances, showed the best oxidation activity in the range of $pH < 3$, $3 < pH < 8$ and $pH > 8$, respectively [27]. In this paper, the effect of initial pH on acrylonitrile removal was studied in the range of 2-11.

FIG. 4a showed the relationship between pH and acrylonitrile concentration. When the pH was 9.00 and the reaction time was 40

min, the acrylonitrile content was zero, indicating the removal rate of acrylonitrile was 100%, and the degradation reaction rate of acrylonitrile was the highest (0.49 mmol/L/min as shown in **Table 2**), and this may be because the yield of oxidative active particles such as active chlorine and hydroxyl radical ($\cdot\text{OH}$) was very high when the pH was 9.00. When the pH was 2.06 and 11.00, the removal effect of acrylonitrile was relatively good, mainly due to the acrylonitrile's hydrolysis under the condition of strong acid and strong alkali. When the pH was between 4.00 and 5.67, the acrylonitrile content changes little, that is, the acrylonitrile removal rate was the lowest because the hydrolysis degree was not high, what's more, the higher H^+ concentration neutralized the active oxidation substances.

According to the influence of pH on acrylonitrile concentration in **FIG. 4a**, the kinetic equation, linear correlation coefficient, the reaction rate and half-life (reaction time required when acrylonitrile removal rate was 50%) of acrylonitrile concentration and reaction time at various pH were shown in **TABLE 2**, and the relationship between pH and reaction rate was displayed in **FIG. 4b**.

TABLE 2. Kinetics of the removal of acrylonitrile.

Parameter		Kinetic equations	R^2	Reaction rate	$t_{1/2}$
pH	2.06	$y = -0.42x + 16.95$	0.945	0.42	20.12
	4	$y = -0.39x + 18.94$	0.992	0.39	24.06
	5.67	$y = -0.40x + 20.04$	0.956	0.4	24.78
	9	$y = -0.49x + 18.71$	0.991	0.49	19.22
	11	$y = -0.42x + 17.53$	0.971	0.42	20.84
Voltage	7	$y = -0.20x + 18.99$	0.951	0.2	47.21
	8.5	$y = -0.20x + 19.23$	0.986	0.2	49.33
	10	$y = -0.50x + 19.00$	0.989	0.5	19.18
	12.5	$y = -0.48x + 17.93$	0.978	0.48	18.58
	15	$y = -0.51x + 18.96$	0.977	0.51	18.76
Current	0.3	$y = -0.21x + 18.48$	0.968	0.21	43.95
	0.5	$y = -0.27x + 18.30$	0.975	0.27	34.18
	0.75	$y = -0.35x + 17.70$	0.964	0.35	25.48

Combined with **FIG. 4b** and **TABLE 2**, when the reaction time was less than or equal to 40 min, the concentration of acrylonitrile had an approximate linear relationship with the reaction time under the same pH, with a high linear correlation coefficient (> 0.9), indicating that the electro-catalytic removal law of acrylonitrile accorded with the zero-order reaction, that is, the reaction rate was not affected by the acrylonitrile concentration. The effect of pH on the oxidation removal rate of acrylonitrile was complicated. The reaction rate of acrylonitrile first decreased and then increased, and again decreased with the increase of pH. The maximum removal rate of acrylonitrile (0.49 mmol/L/min) was achieved when pH was 9.00, at this time, the required time was 19.22 min as the removal rate of acrylonitrile was 50%.

The effect of voltage

In the process of electro-catalytic oxidation, the voltage can affect the current and the electric field strength influencing the directional migration of charged ions, and then affect the formation of active substances in water, which was reflected in the change of pollutant content. According to the influence of the voltage on acrylonitrile concentration in **FIG. 4c**, the kinetic equation, linear correlation coefficient, the reaction rate and half-life (reaction time required when acrylonitrile removal rate was 50%) of acrylonitrile concentration and reaction time under each voltage were illustrated in **TABLE 2**, and the relationship between the voltage and reaction rate was shown in **FIG. 4d**.

FIG. 4c and 4d depicted the influence of the voltage on the oxidation removal effect of acrylonitrile at an initial acrylonitrile concentration of 18.85 mmol/L and the chlorine concentration of 5000 mg/L with the Mn/Sn doping Ru-Ir electrode as anode. The influence of the voltage on the oxidation removal rate of acrylonitrile was complicated. Under the same voltage, the removal rate

of acrylonitrile continuously increased with the increase of reaction time. As shown in **FIG. 4c** and **TABLE 2**, there was an approximate linear relationship between acrylonitrile concentration and reaction time at the same voltage as the reaction time was less than or equal to 40 min, with a high linear correlation coefficient (> 0.9), explaining that the electro-catalytic removal law of acrylonitrile conformed to the zero-order reaction, that is, the reaction rate was not affected by acrylonitrile concentration. The removal rate of acrylonitrile increased from 40.36% to 100% at the reaction time of 40 min, what's more, the reaction rate of acrylonitrile oxidation removal increased from 0.20 mmol/L/min to 0.50 mmol/L/min with the voltage changing from 8.5 V to 10.0 V, because the yield of effective active substances in the solution increased with the increase of the voltage, promoting the significant removal of acrylonitrile. However, when the voltage was less than 8.5 V or greater than 10.0 V, changing the voltage had little impact on the removal rate of acrylonitrile. As the voltage was 7.0 V and 8.5 V, the removal rate of acrylonitrile was 52.39% and 53.47% at the reaction time of 50 min, respectively, in addition, the reaction rate of oxidation removal of acrylonitrile was basically unchanged at about 0.20 mmol/L/min, and the average half-life was 48.27 min, which may be due to the low yield of effective active substances. As the voltage fluctuated between 10.0 V and 15.0 V, the reaction rate of acrylonitrile oxidation removal was basically unchanged, maintaining about 0.50 mmol/L/min, the average half-life was 18.84 min, and the removal rate of acrylonitrile varied little, but the energy consumption was increased. On the one hand, side reactions occurred on the electrode surface, such as oxygen evolution reaction, causing the content of effective active oxidizing species not to accumulate with the increase in higher voltage; On the other hand, from the kinetic point of view, the electrocatalytic oxidation process entered the diffusion control stage, at which time the reaction rate was affected by the stirring rate or the initial concentration of reactants, when the voltage reached a critical value. Based on this, it can be concluded that the optimal voltage range was 8.5 V~10.0 V during the process of electro-catalytic oxidation for acrylonitrile removal.

The effect of current

The current was an important parameter affecting the electro-catalytic oxidation process, determining the migration ability of electrons and the generation rate of active substances (such as Cl_2 , HClO , ClO^- , Cl , OH , HO_2^- and O_2^- , etc.).

According to the influence of the current on acrylonitrile concentration in **FIG. 4e**, the kinetic equation, linear correlation coefficient, the reaction rate and half-life (reaction time required when acrylonitrile removal rate was 50%) of acrylonitrile concentration under each current were shown in **TABLE 2**, and the relationship between current and reaction rate was displayed in **FIG. 4f**.

FIG. 4e illustrated the influence of the current on the oxidation removal effect of acrylonitrile when the initial concentration of acrylonitrile was 18.85 mmol/L and the chloride ion concentration was 5000 mg/L with Mn/Sn doping Ru-Ir electrode as anode. The current can obviously promote the oxidative removal of acrylonitrile. As the current was 0.30 A, 0.50 A and 0.75 A, the removal rates of acrylonitrile at the reaction time of 50 min were 61.85%, 74.60% and 90.88%, respectively, because the higher current was more beneficial to the yield of active oxidizing substances, and then more conducive to the removal of acrylonitrile. Combined with **FIG. 4e** and **TABLE 2**, the concentration of acrylonitrile had an approximate linear relationship with the reaction time under the same current, and the high linear correlation coefficient (>0.9) explained that the electro-catalytic removal of acrylonitrile accorded with the zero-order reaction, that is, the reaction rate was not affected by the concentration of acrylonitrile. Besides, when the current was 0.30 A, 0.50 A and 0.75 A, the reaction rates of acrylonitrile oxidation were 0.21 mmol/L/min, 0.27 mmol/L/min and 0.35 mmol/L/min respectively, and the half-lives were 43.95 min, 34.18 min and 25.48 min, respectively. In combination with **FIG. 4f**, the reaction rate of acrylonitrile oxidation was positively correlated with the current, and the relationship formula was as follows:

$$y = 0.31x + 0.12 \quad R_2 = 0.9997 \quad (5)$$

Where x and y represented the current (A) and the reaction rate of acrylonitrile (mmol/L/min), respectively. According to formula (5), the higher the current was, the higher the oxidation reaction rate of acrylonitrile would be. However, from the perspective of energy consumption, excessive current will increase the energy consumption of wastewater treatment and increase the cost of wastewater treatment. Therefore, the current should be controlled at 0.30 A-0.75 A to maintain a high reaction rate of acrylonitrile removal in the process of electro-catalytic oxidation of acrylonitrile wastewater.

RSM design

2FI model: According to the 3-factor and 3-level experiments designed by RSM, 13 groups of experiments were carried out, and the experimental results were shown in **TABLE 3**. The influence of multi-factors on acrylonitrile removal efficiency was analyzed by using Design-Expert software, and the optimal multi-factor interaction equation was obtained as follows:

$$y = 378.93 - 187.31 * x_1 - 4.88 * x_2 - 34.47 * x_3 + 2.05 * x_1 x_2 + 15.90 * x_1 x_3 + 0.49 * x_2 x_3 \quad (6)$$

Where, y represented the removal rate of acrylonitrile (%), x_1 , x_2 and x_3 were current, reaction time and pH, respectively.

TABLE 3. Experimental results of acrylonitrile removal by electro-catalytic oxidation.

Times	The current/A	Reaction time/min	pH	The removal rate of acrylonitrile/%
1	1	50	9	95.51
2	0.75	30	11	51.67
3	1	30	9	71.16
4	1	40	7	88.67
5	0.5	40	7	73.82
6	0.5	50	9	78.16
7	0.5	40	11	43.65
8	1	40	11	90.3
9	0.75	40	9	82.22
10	0.5	30	9	74.31
11	0.75	50	11	100
12	0.75	30	7	80.46
13	0.75	50	7	89.57

On the basis of experimental values, Fisher test was used for statistical test of variance analysis of regression parameters in 2FI model. It was significantly consistent with the 2FI model according to the experimental results displayed in TABLE 4, because the F value of the model was 5.18, which was relatively large, the value of Prob > F was less than 0.05, and the correlation coefficient R^2 can reach 0.84.

TABLE 4. The variance analysis results by RSM.

Source	Mean square	F Value	p-value Prob > F	
Model	441.75	5.18	0.0328	significant
x_1	716.27	8.39	0.0274	significant
x_2	916.79	10.74	0.0169	significant
x_3	274.93	3.22	0.1228	
$x_1 x_2$	105.11	1.23	0.3096	
$x_1 x_3$	252.95	2.96	0.1359	
$x_2 x_3$	384.44	4.5	0.078	

Optimum reaction condition

According to the RSM experiment, the optimum conditions for acrylonitrile removal were as follows: pH 10.12, current 0.81 A and reaction time 39.64 min. In order to further verify the accuracy and reliability of the real model, the pH, current and reaction time were changed, and the experiment was conducted again to compare the relationship between the actual value and predicted value of acrylonitrile removal rate. As shown in TABLE 5, the maximum error of acrylonitrile removal rate between the actual value and the predicted value was 2.01, indicating that the predicted value was in good agreement with the experimental value, illustrating that the 2FI model formula (6), had good accuracy and reliability, and that RSM was a powerful tool for optimizing the operating conditions of electrochemical experiments with high accuracy.

TABLE 5. 2FI model validation data and reaction results.

Times	Current A	Reaction time min	pH	Actual removal rate %	Predicted removal rate %	Error
1	0.6	35	8	74.54	76.55	2.01
2	0.9	35	8	79.68	80.05	0.37
3	0.8	45	10	84.78	86.28	1.5

The interaction between factors

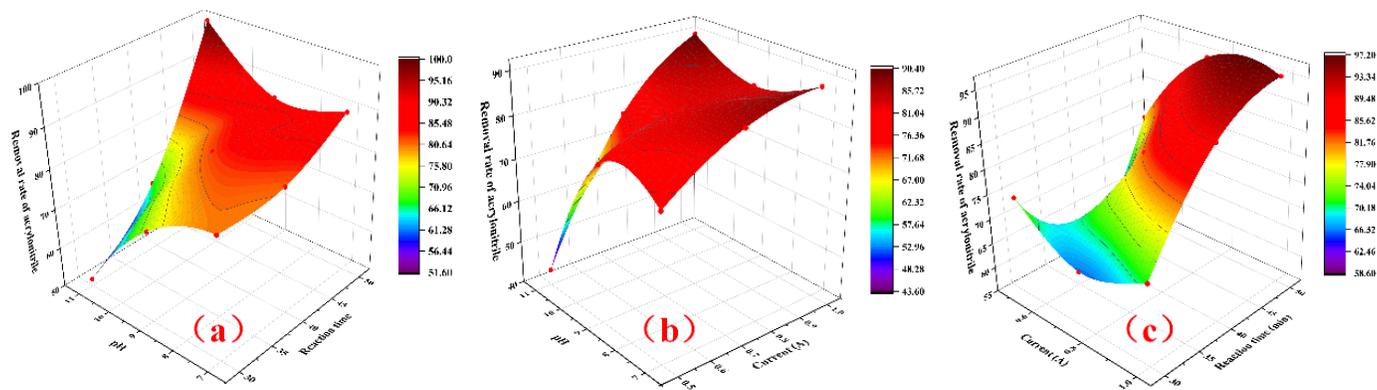


FIG. 5. The interaction between pH, reaction time and current

FIG. 5a displayed the effect of pH and reaction time on acrylonitrile removal rate. As the reaction time was less than or equal to 40 min, the removal rate of acrylonitrile decreased with the increase of pH at the same reaction time, and this results may declare that the higher concentration of OH⁻ can make the active chlorine (chlorine gas and hypochlorite etc.) with higher oxidation properties transform into the active chlorine (hypochlorite) with lower oxidation properties, reducing the removal rate of acrylonitrile. When the reaction time was greater than 40 min, the removal rate of acrylonitrile increased with the increase of pH at the same reaction time, and this phenomenon may explain that the extension of time increased the contact opportunity between acrylonitrile and active oxidation substances, promoting the removal of acrylonitrile. Besides, the reaction time had little effect on the removal rate of acrylonitrile as the pH of acrylonitrile was 7 (neutral). However, the removal rate of acrylonitrile continued to increase with the increase of reaction time at the same pH during the pH was greater than 7 (alkaline).

FIG. 5b depicted the effect of pH and current on acrylonitrile removal rate. The removal rate of acrylonitrile decreased with the increase of pH due to the decrease of active oxidizing substances for the excess of OH⁻ when the current was less than or equal to 0.8 A. The removal rate of acrylonitrile increased with the increase of pH at the same current as the current was greater than 0.8 A, and this results specified that the conversion of OH⁻ into [•]OH was promoted under high current, improving the removal of acrylonitrile. However, the current had little effect on the removal rate of acrylonitrile in a neutral environment (pH = 7). While the pH was greater than 7 (alkaline), the removal rate of acrylonitrile continued to increase with the increase of current at the same ph.

FIG. 5c illustrated the effects of current and reaction time on acrylonitrile removal rate. Under any conditions of reaction time and current, the removal rate of acrylonitrile increased with the increase of reaction time and current, indicating that current and reaction time always have a good synergistic promoting effect on the removal of acrylonitrile.

Mechanism of electro-catalytic degradation of acrylonitrile

Electro catalytic oxidation pathway

Were basically similar at different scanning speeds. When the scanning speed was 5 mV/s and the voltage scanning FIG. 6 showed the CV curves of Mn/Sn doping Ru-Ir electrode in a solution of 5000 mg/L chloride ion and 1000 mg/L acrylonitrile. The shapes of scanning curves range was 0 V~1.5 V, the current increased instantaneously and a large peak appeared only after 1.0 V in FIG. 6a, attributing to the generation of chlorine gas. Taking the scanning speed of 100 mV/s and the voltage range of -1.2 V~1.2 V as

an example (shown in **FIG. 6b**), when the voltage was greater than 0 V, an obvious small peak appeared around 0.6 V at the forward scanning speed; In reverse scanning, a small peak appeared at about 0.5 V, and the peak value became smaller obviously. What's more, the peak at about 0.6 V was basically opposite to the peak around 0.5 V, and this phenomenon emphasized the adsorption-desorption process of acrylonitrile. Moreover, the peak value around 0.6 V was obviously larger than the peak value around 0.5 V, indicating that some acrylonitrile after adsorption had undergone oxidative decomposition reaction, resulting in a decrease in the peak value during acrylonitrile desorption. In conclusion, there were adsorption-desorption process of acrylonitrile and oxidation reaction of acrylonitrile on the electrode surface, and chlorine gas generation reaction in the process of treating acrylonitrile simulated wastewater by electro catalysis technology.

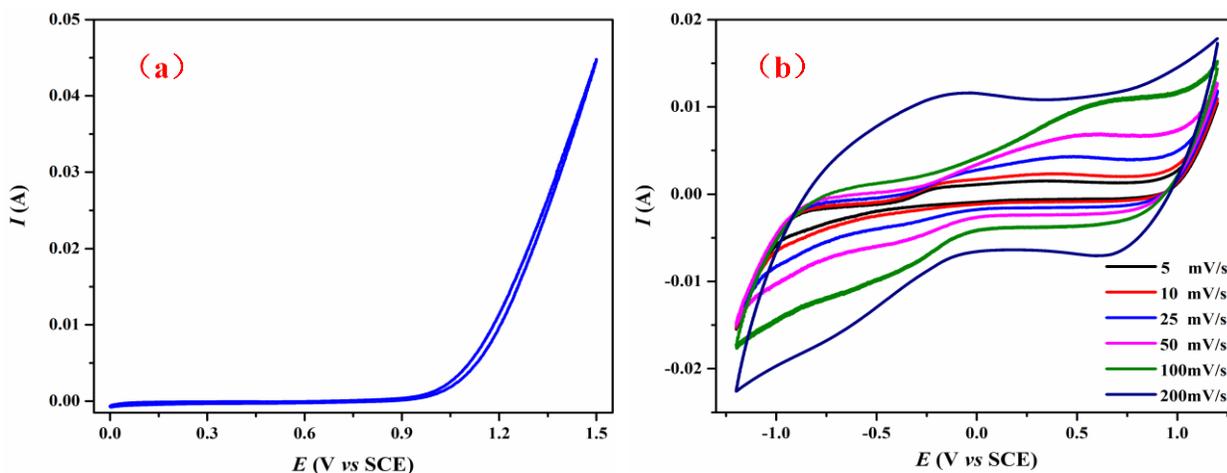


FIG. 6. CV curves of acrylonitrile simulated wastewater (a) Scanning speed 5 mV/s, voltage 0 V~1.5 V; (b) Scanning speed 5 mV/s ~200 mV/s, voltage -1.2 V~1.2 V.

The Nyquist diagram of Mn/Sn doping Ru-Ir electrode in the solution of 5000 mg/L chloride ion and 1000 mg/L acrylonitrile (Z' is the real part and Z'' is the imaginary part) was displayed in **FIG. 7a**. At 1.2 V, the impedance diagram was arc-shaped, indicating that the control stage of electro-catalytic oxidation to remove acrylonitrile was in charge transfer control stage; At 1.15 V, the impedance diagram was arc-shaped, but the radius of the arc increased obviously, showing that the treatment process of acrylonitrile simulated wastewater changed from the charge transfer control stage to the solution mass transfer control stage at this voltage; When the voltage was between 1.0 V and 1.1 V, the impedance diagram was basically in the form of a straight line, and the reaction of removing acrylonitrile by electro-catalytic oxidation was in the stage of mass transfer control. As the slope of the straight line was less than 45° , it declared that there was a diffusion barrier layer on the electrode surface during the electro-catalytic treatment of acrylonitrile simulated wastewater. According to this analysis, the voltage should be controlled above 1.2 V at least in the process of acrylonitrile removal by electro-catalytic oxidation, so that the control stage of electro-catalytic oxidation to remove acrylonitrile was in the charge transfer control stage, and then the charge amount can be adjusted by means of adjusting the current, so as to achieve the purpose of regulating the effect of acrylonitrile removal by electro-catalytic oxidation.

NaCl (5000 mg/L Cl^-) and Na_2SO_4 (10000 mg/L) were used as electrolytes to investigate the effect of indirect oxidation and direct oxidation on acrylonitrile removal rate with Mn/Sn doping Ru-Ir electrode as anode (shown in **FIG. 7b**). The initial acrylonitrile concentration was 1000 mg/L. The removal rate of acrylonitrile increased with the increase of reaction time, and the removal rate of acrylonitrile with NaCl as electrolyte was higher than that with Na_2SO_4 as electrolyte. As the acrylonitrile removal rate with NaCl as electrolyte reached 100% at 40 min, the fitting straight line a of acrylonitrile removal rate with NaCl as electrolyte in the first 40 min was shown in Formula (7):

$$y = 2.50x + 5.05 \quad R_2 = 0.977 \quad (7)$$

The fitting line b of acrylonitrile removal rate with Na_2SO_4 as electrolyte was revealed in Formula (8):

$$y = 1.81x - 3.67 \quad R_2 = 0.972 \quad (8)$$

According to formulas (7) and (8), the rate constants of acrylonitrile removal were 2.50 min^{-1} and 1.81 min^{-1} , respectively, highlighting that NaCl was more conducive to the rapid removal of acrylonitrile on account of the combined effect of direct and

indirect oxidation. In the presence of NaCl, possible reactions occurred on the electrode surface as follows [30-32]:



According to Eqs (9)-(14), the oxidation active species produced by electrocatalysis included $Cl_2(aq.)$, $\cdot Cl$, $HClO$, $\cdot OCl$ and ClO^{-} , etc. obtaining stronger reactivity to indirectly degrade organic matters [27]. On the other hand, the removal rate of acrylonitrile directly degraded by electrodes attained 71.50% at 40 min in the presence of Na_2SO_4 . Consistent with the fact that the electrocatalytic oxidation of acrylonitrile was completed by direct oxidation coupled with indirect oxidation. For instance, the removal rates of acrylonitrile by direct oxidation and indirect oxidation at 40 min accounted for about 70% and 30% respectively.

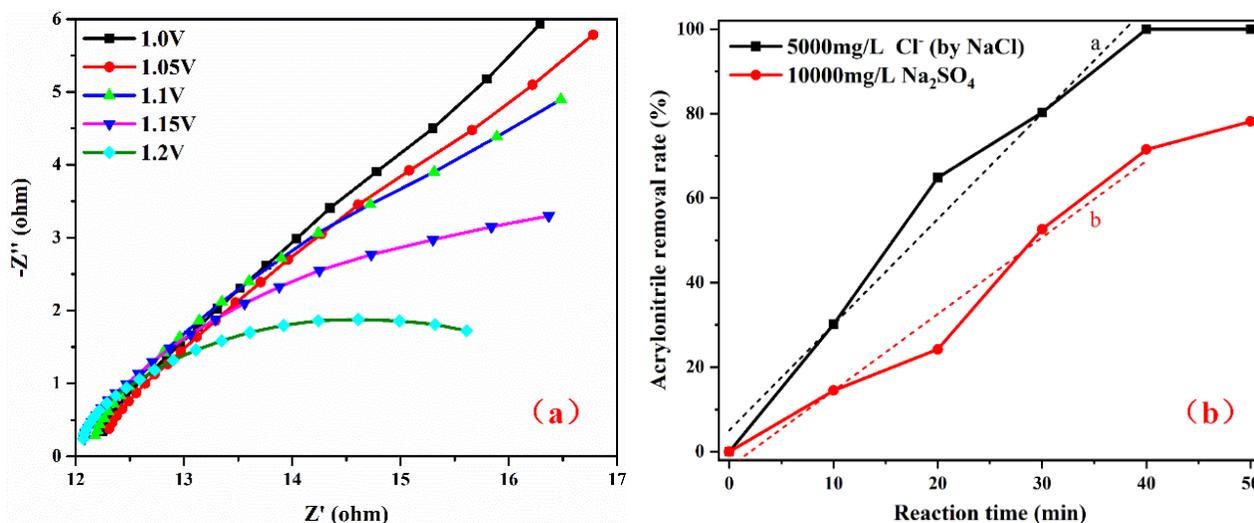


FIG. 7. (a) Nyquist plot of acrylonitrile wastewater; (b) the influence of electrolytes on acrylonitrile simulated wastewater treatment was investigated with Mn/Sn doping Ru-Ir electrode as anode and NaCl and Na_2SO_4 as electrolytes, respectively (dotted line is the fitting regression line relationship).

Analysis of Reactive oxygen species (ROS)

FIG. 8a depicted the changes of free chlorine, bound chlorine and total chlorine content during the oxidation of acrylonitrile by Mn/Sn doping Ru-Ir electrode in the solution of 5000 mg/L chloride ion and 1000 mg/L acrylonitrile. Free chlorine referred to chlorine in the form of hypochlorous acid, hypochlorite ion and dissolved elemental chlorine; Bound chlorine referred to chlorine in the form of chloramine and organic chloramine; Total chlorine referred to chlorine in the form of "free chlorine" or "bound chlorine", or the coexistence of both. The contents of free chlorine and total chlorine both increased with the increase of time, but the rate of total chlorine increase was greater than that of free chlorine, and the difference between them was the content of bound chlorine, indicating that the content of bound chlorine continued to increase with the increase of time, and the growth rate of bound chlorine was the fastest when the reaction time was 10 min-30 min. At 50 min, the contents of free chlorine, bound chlorine and total chlorine were 0.5649mmol/L, 2.4177mmol/L and 2.9826 mmol/L, respectively. To sum up, chlorine-containing oxidation active substances can promote the denitrification of acrylonitrile, and some organic nitrogen in acrylonitrile will be converted into compound chlorine (chloramine and organic chloramine) in the process of removing acrylonitrile by electrocatalytic oxidation.

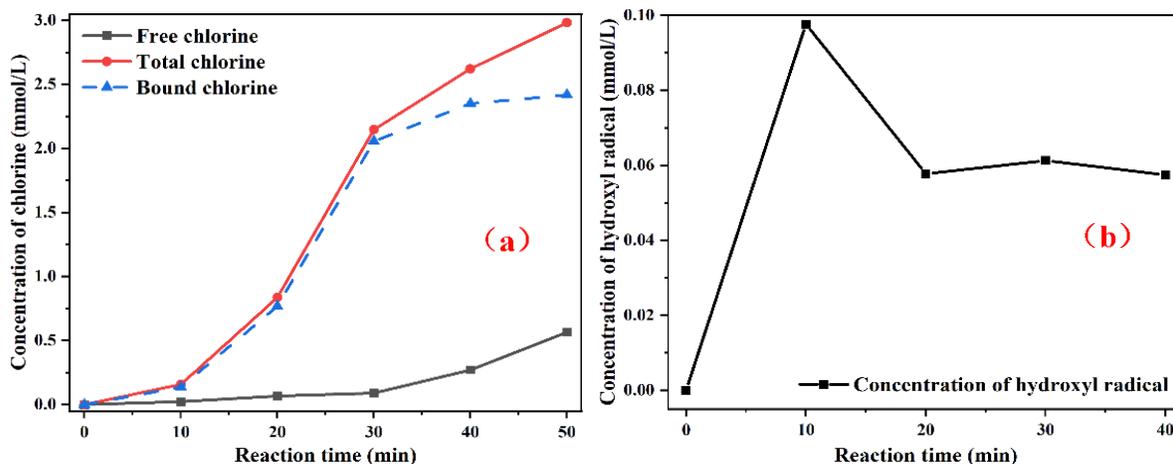


FIG. 8. (a) Changes in free chlorine, bound chlorine and total chlorine content; (b) hydroxyl radical content

FIG. 8b presented hydroxyl radical content of acrylonitrile removed by Mn/Sn doping Ru-Ir electrode in the solution of 5000 mg/L chloride ion and 1000 mg/L acrylonitrile. The maximum content of hydroxyl radical was about 0.10 mmol/L, far less than 1.20 mmol/L (**FIG. 2**), indicating that hydroxyl radical participated in the electrocatalytic oxidation of acrylonitrile. The hydroxyl radical may directly mineralize the acrylonitrile and be consumed by the chloride species. What's more, the content of hydroxyl radical was basically stable and maintained at about 0.06 mmol/L with the extension of time on account of the fact that the production and consumption of hydroxyl radical were basically equal as the reaction time was more than 20 min. These results declared that hydroxyl radical was one of the oxidation substances to remove acrylonitrile.

The analysis of products

FIG. 9a described nitrogen-containing products and their contents during the oxidation of acrylonitrile with Mn/Sn doping Ru-Ir electrode in a solution of 5000 mg/L chloride ion and 1000 mg/L acrylonitrile. The electro-catalytic oxidation products of acrylonitrile contained nitrite nitrogen and nitrate nitrogen, however ammonia nitrogen had not been detected during the reaction, indicating that oxidizing substances such as active chlorine may directly attack the triple bond of carbon and nitrogen, and transform organic nitrogen into nitrogen compounds in the form of non-ammonia nitrogen. The content of nitrite nitrogen fluctuated greatly with the increase of reaction time, increasing from zero to 15.87 mg/L at 50 min. Besides, the removal rate of TN continued to increase, reaching 85.87% at 50 min, declaring that the electro-catalytic oxidation of acrylonitrile had high nitrogen removal performance.

FIG. 9b was a graph of TOC content of acrylonitrile oxidized by Mn/Sn doping Ru-Ir electrode in a solution of 5000 mg/L chloride ion and 1000 mg/L acrylonitrile. The organic carbon can be converted into inorganic carbon in the process of removing acrylonitrile by electro-catalytic oxidation. With the increase of reaction time, the removal rate of TOC gradually increased, attaining 72.40% at 50 min, declaring that electrocatalysis technology could effectively mineralize acrylonitrile.

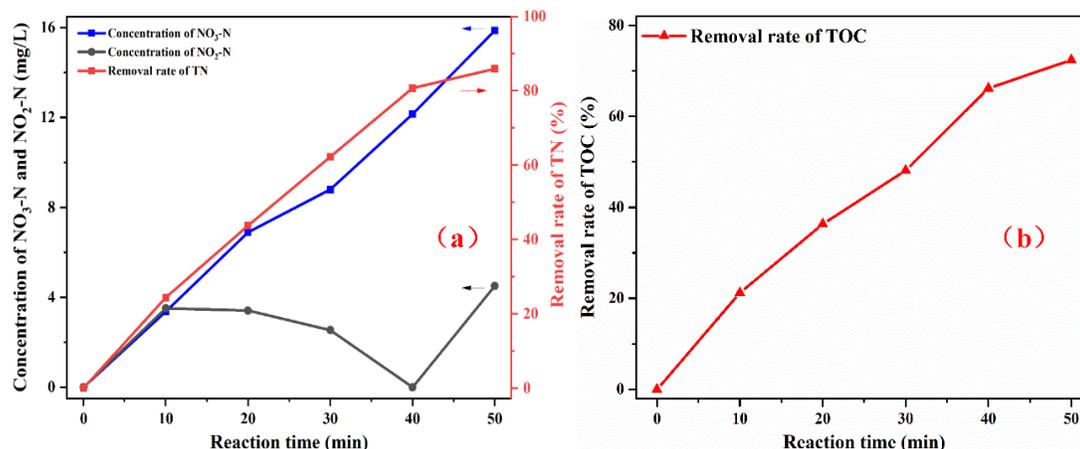


FIG. 9. (a) Nitrogen products and their contents; (b) changes in TOC content

In order to evaluate the evolutions of organic components before and after the electro-catalytic reaction of acrylonitrile simulated wastewater, the gas chromatography-mass spectrometry system (GC-MS) was used to analyze the organic components. **FIG. 10** illustrated the GC-MS spectra of the simulated acrylonitrile wastewater treated by electro catalysis under different reaction time. Acetone, Acrylonitrile and Hydroxy acetic acid ($C_2H_4O_3$) were detected during the retention time of 2 min to 3 min, with organic compounds matching 97%, 98% and 89%, respectively. With the reaction exceeded, the peak area of acrylonitrile decreased to 0 continuously, indicating that electrocatalytic degradation can effectively remove acrylonitrile. However, the fluctuation of acetone peak area was small, suggested that acetone was not produced in the process of electro-catalytic removal of acrylonitrile. It was worth noting that hydroxyacetic acid was detected after 30 min, and the peak area of hydroxyacetic acid continued to increase with the increase of reaction time, indicating that hydroxylacetic acid was produced and accumulated as the reaction intermediates. This result was agrees the partial mineralization of TOC. The produced hydroxyacetic acid had good biodegradability and could be removed by subsequent biochemical systems.

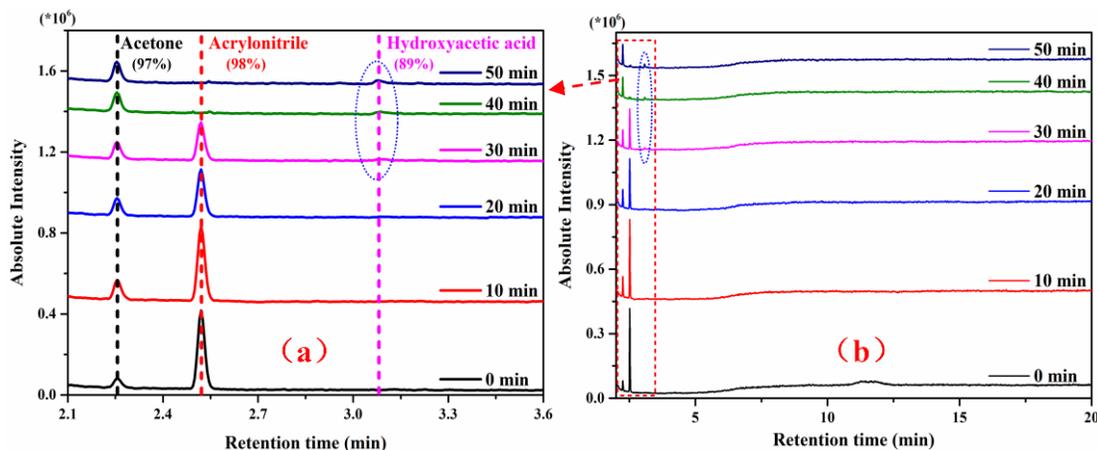


FIG. 10. GC-MS total ion chromatogram of electrocatalytic oxidation of acrylonitrile at different reaction times. (a) Retention time 2.1 min-3.0 min, (b) Retention time 2 min-20min.

The proposed reaction process

On basis of above results, free chlorine and hydroxyl radicals were produced during the electrocatalysis, and acrylonitrile especially undergone the adsorption-desorption process on the surface of Mn/Sn doping Ru-Ir electrode. The following reaction process was thus speculated: Acrylonitrile gained and loosed electrons on the electrode surface to be directly degraded. Acrylonitrile can also be directly oxidized by hydroxyl radicals adsorbed on the electrode surface ($\cdot OH_{ads}$) [27]. In addition, free chlorine and hydroxyl free radicals ($\cdot OH_{free}$) desorbed from the electrode surface can indirectly mineralize acrylonitrile. The proposed reaction process of electro-catalytic treatment of acrylonitrile was presented in **FIG. 11**.

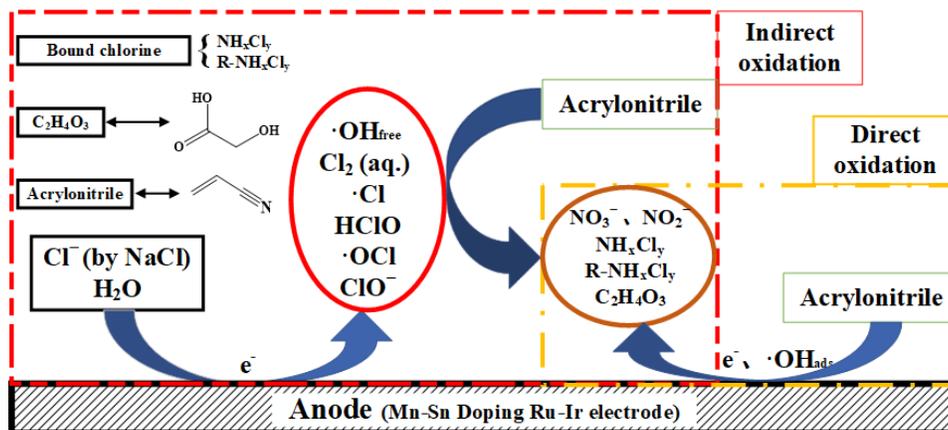


FIG. 11. The proposed reaction process of electro catalytic treatment of acrylonitrile.

Conclusions

This paper demonstrates that the electro-catalytic technology with Mn/Sn doping Ru-Ir electrode as anode can efficiently treat acrylonitrile simulated wastewater. The main conclusions were as follows:

Compared with Ru-Ir electrode, Mn/Sn doping Ru-Ir electrode had higher oxygen evolution potential (1.3278 V vs. SCE) and lower chlorine evolution potential (1.1243 V vs. SCE); (2) the influence of voltage, current and pH on acrylonitrile removal accorded with the zero-order kinetic equation. RSM was used to analyze the influence of many factors on acrylonitrile simulated wastewater. The results indicated that the optimal conditions for electro-catalytic treatment of acrylonitrile were pH 10.12, reaction time 39.64 min and current 0.81 A. The influence of multiple factors on acrylonitrile removal rate conformed to the 2FI model; (3) There were adsorption-desorption process and catalytic oxidation process on the electrode surface in the process of electro-catalytic removal of acrylonitrile, but there was a particle diffusion barrier layer between the electrode and the solution. Electro-catalytic removal of acrylonitrile was the result of direct oxidation and indirect oxidation. When the reaction volume was 200 mL, the concentration of chloride ion was 5000 mg/L, the concentration of acrylonitrile was 1000 mg/L, the reaction time was 50 min, and the current was 1 A, the removal rate of acrylonitrile can reach 100%, among which the nitrogen removal rate can reach 85.87%, and the mineralization rate of organic matter can reach 72.40%. The organic product was hydroxyl acetic acid with good biodegradability. In conclusion, the electro-catalytic technology was convenient and efficient to treat acrylonitrile wastewater with the effect of denitrification and organic mineralization.

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, [Jian Zhao], upon reasonable request.

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