Optimization of the Electrochemical Treatment of 4-chlorophenol Wastewater Using Response Surface Method

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ABSTRACT
Chlorophenols (CPs) are a kind of important organic chemical intermediates, which are produced in various industrial processes. Currently, electrochemical method is the most effective treatment for the degradation of chlorophenols (CPs) in wastewater. In this study, a three-dimensional electrode electrochemical reactor, constructed using the Sn/Sb-Mn-GAC (granular activated carbon) particle electrodes, was used to treat the wastewater containing 4-chlorophenol. On the basis of single factor experiments, the process conditions of the designed three-dimensional electrochemical reactor were optimized using the response surface methodology. The experimental results showed that the three-dimensional electrochemical reactor could effectively reduce 4-chlorophenol by 96.13% at the optimum Na2SO4 concentration of 2 g·L−1, electrode plate distance of 2 cm, current intensity of 2 A, and particle electrode dosage of 14 g. The experimental observations were in reasonable agreement with the modeled values, thus verifying the design of the proposed reactor.

Keywords : Electrochemical, Particle Electrode, 4-chlorophenol, Response Surface

1. Introduction
Chlorophenols (CPs) are a kind of important organic chemical intermediates and have the characteristics of high toxicity and refractory degradation.1 They mainly originate from industrial production and processing industry, such as printing and dyeing, leather, pharmaceuticals, paper making, textiles, and coatings.2−4 If chlorophenols are released into the environment without being completely or partially degraded, they will pose a great threat to water quality of rivers, soils and groundwater.5 Chlorophenols have been listed as priority pollutants by the European Environmental Agency (EEA).6 Additionally, chlorophenol was listed as a controlled toxic substance by the Emergency Planning and Community Right-to-Know Act (EPCRA) that was approved by the US Congress in 1986.7 The U.S. Environmental Protection Agency (USEPA) has issued strict regulations to classify the twenty-five (25) chlorophenols as priority pollutants and has stipulated that the contents of 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) in surface water should not exceed 81 µg·L−1, 77 µg·L−1, 1.4 µg·L−1 and 0.27 µg·L−1, respectively.8 Similarly, 2-CP, 2,4-DCP, 2,4,6-TCP and PCP are listed as the main toxic organic pollutants under priority control in groundwater environment in China.

Nowadays, the treatment methods of phenolic wastewater are classified into microorganism methods, physicochemical methods, and chemical oxidation methods. The microorganism treatment technology is adopted to degrade chlorophenols in wastewater. Suitable microorganisms are selected to treat chlorophenols using the microbial treatment technology, in which chlorophenols were used as the carbon and energy sources. Under certain growth conditions, chlorophenols in wastewater were removed to treat the wastewater using microbial metabolism. However, the treatment of chlorophenols by microorganisms is a long process. Armenante et al. studied the treatment of wastewater containing 2,4,6-TCP using the anaerobic/aerobic process,9 and reported that 2,4,6-TCP was reduced, while the chlorine atoms on 2,4,6-TCP were removed to form 2,4-dichlorophenol and 4-chlorophenol. When the reaction entered the aerobic stage, aerobic microorganisms could completely degrade 4-chlorophenol and 2,4-dichlorophenol, from which the chlorine atoms had been removed. Arora et al. studied the degradation of chlorophenols under aerobic and anaerobic conditions,10 and found that, under aerobic conditions, chlorohydroquinone or chlorocatechol formed during the action of microorganisms, and participated in the tricarboxylic acid cycle. Furthermore, under anaerobic conditions, chlorophenol pollutants were converted to phenols by reduction and dechlorination. Moreover, phenol was oxidized and converted to benzoic acid, which was eventually oxidized to carbon dioxide (CO2).

In addition, the physicochemical methods were used to treat chlorophenol pollutants in wastewater systems. In order to degrade chlorophenol pollutants in wastewater, the most commonly used method was the solid adsorption. However, chlorophenols could not be effectively decomposed using the adsorption method. Therefore, it would cause accumulation of solid waste. Hameed et al. studied the adsorption process of 2,4,6-trichlorophenol in wastewater using coconut shell-activated carbon,11 and found that Langmuir model could describe the process of adsorption on coconut shell-activated carbon. Mubarak et al. used bagasse as raw material to prepare a cylindrical porous material with large surface area,12 and reported that the maximum adsorption capacity of bagasse-activated carbon for the adsorption of 2,4,6-TCP in wastewater was 253.38 mg/g. Furthermore, 2,4,6-TCP could be effectively degraded in the presence of a variety of toxic organic substances. Ren et al. used phosphoric acid-activated plant fibers to prepare the activated carbon,13 which contained multiple groups, such as hydroxyl, lactone and carboxyl. The specific surface area of the prepared activated carbon was as high as 890.27 m2/g, and the removal efficiencies of 2,4-DCP and 2,4,6-TCP in wastewater were very high.
Granular activated carbon (GAC) is an industrial adsorbent, and can be divided into two classes, namely the fixed and non-fixed particles. It is mainly made of coconut shell, fruit shell and coal. These raw materials undergo a series of production processes using precise machining. Granular activated carbon (GAC) has developed porous structure, good adsorption performance and good regeneration performance. It can be widely used in various fields, such as purification of drinking water, purification of gases, desiccant preparation, and solvent recovery.

Reasonable design of an electrochemical reactor and its process conditions not only save energy and reduce costs, but also result in high efficiency of pollutant removal. Three-dimensional electrode technology is a new type of electrochemical technology. It is used to fill granular working electrode materials between the two-dimensional electrolyzer electrodes, and convert the surface of the charged working material into a new electrode (the third electrode). The electrochemical reaction occurs on the surface of the electrode materials.

Currently, advanced oxidation technology has been widely and successfully used to treat large amounts of wastewater, including landfill leachate, dye wastewater, paper-making wastewater, tannery wastewater, and wastewater containing chlorophenols. Three-dimensional electrochemical reactor consists of electrolytic tank, paired electrodes and particle electrodes. Particle electrodes are dimensionally electrochemical reactor and its process conditions not only save energy and reduce costs, but also result in high efficiency of pollutant removal. Three-dimensional electrode technology is a new type of electrochemical technology. It is used to fill granular working electrode materials between the two-dimensional electrolyzer electrodes, and convert the surface of the charged working material into a new electrode (the third electrode). The electrochemical reaction occurs on the surface of the electrode materials.

During the removal of pollutants, the pollutants are moved to the periphery of the molecular layer of particle electrodes under the action of electric field and charge. The flow of electrons degrades the targeted substances through intramolecular ring opening reaction and chain-breaking reactions, thus degrading the pollutants in the system. The oxidation process consists of the direct oxidation and indirect oxidation. During the process of direct oxidation, the organic pollutant R is degraded through metal electrocatalytic intermediate products MOx-1 and MOx(OH). As a result, reactive oxygen species are formed during the electrocatalysis of metal oxide MOx. The chemical reactions for the formation of two reactive oxygen species on the surface of electrode are given by Eqs. (1) and (2).

\[
\begin{align*}
\text{MO}_x + H_2O & \rightarrow \text{MO}_x(OH) + H^+ + e^- \quad (1) \\
\text{MO}_x(OH) & \rightarrow \text{MO}_{x-1} + H^+ + e^- \quad (2)
\end{align*}
\]

During the reaction between the catalytic intermediate products and the organic substance R, the electrochemical intermediate products are formed. The corresponding chemical reactions are given by Eqs. (3) and (4).

\[
\begin{align*}
\text{R} + \text{MO}_x(OH) & \rightarrow \text{CO}_2 + H^+ + \text{MO}_x + e^- \quad (3) \\
\text{R} + \text{MO}_{x+1} & \rightarrow \text{MO}_x + \text{RO} \quad (4)
\end{align*}
\]

During the indirect oxidation, active substances such as ·OH, O, O2-, and ClO-, which were formed by the metal oxide MOx on the surface of electrodes, are oxidized and degraded with the organic pollutants, thus reducing the toxicity of the system. During this process, the indirect oxidation reactions of hydroxyl radicals (·OH) are given by Eqs. (5) and (6).

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \cdot\text{OH} + \text{H}^+ + e^- \quad (5) \\
\text{R} + \cdot\text{OH} & \rightarrow \text{CO}_2 + \text{H}^+ + \text{H}_2\text{O} + e^- \quad (6)
\end{align*}
\]

Compared with the traditional treatment process, the process of wastewater treatment using three-dimensional electrode reactor has the advantages of high current efficiency and low energy consumption. Additionally, these beneficial characteristics have far-reaching exploratory value for the application of organic wastewater treatment. In this study, the three-dimensional electrochemical reactor consisted of a DSA plate anode, a titanium plate cathode and an organic glass electrolytic cell. The Sn/Sb-Mn-GAC was used as the particle electrode, whereas the target pollutant was 4-chlorophenol (4-CP) during the experiments. The effects of the concentration of Na2SO4, distance of the electrode plate, current intensity and dosage of particle electrode on the removal efficiency of 4-chlorophenol were investigated using the single factor experiments. On the basis of single factor experiments, the process conditions for the three-dimensional electrochemical reactor constructed using Sn/Sb-Mn-GAC particle electrodes were optimized by response surface methodology. Finally, a quadratic polynomial regression equation was developed to predict the removal efficiency of 4-chlorophenol. The optimum process conditions were obtained and verified using the experimental data.

2. Experimental

2.1 Materials

Granular Activated Carbon (GAC) was obtained from Damao Chemical Reagent Co., Ltd. (China). Mn(NO3)2 was also purchased from Damao Chemical Reagent Co., Ltd. (China). SnCl4·5H2O was obtained from Zhanyun Chemical Reagent Co., Ltd. (China). SbCl3 and anhydrous sodium sulfate were purchased from Chemical Reagent Co., Ltd. (China). Potassium dihydrogen phosphate was obtained from Guanghua Chemical Reagent Co., Ltd. (China). Phosphoric acid was purchased from Guangfu Fine Chemical Co., Ltd. (China). 4-chlorophenol was obtained from Sigma-Aldrich (USA). Acetonitrile was purchased from Merck KGaA (Germany). All other chemicals were of reagent grade and used without further purification.

2.2 Preparation

The granular activated carbon was boiled and washed with a large amount of deionized water. GAC was dried in a baking oven at 105°C. A 200-μL alcohol solution consisting of 40 mg·L⁻¹ SnCl4·5H2O + 10 mg·L⁻¹ SbCl3 + 25 mg·L⁻¹ Mn(NO3)2 was prepared. The 60 g pretreated GAC was soaked in the prepared solution and softened in a shaking table at 150 r/min for 4 hours. Then, the soaked activated carbon was taken out and dried at 105°C. The dried activated carbon was roasted in a muffle oven at 300°C for 2 hours. Finally, the roasted activated carbon was taken out and cooled after firing. The activated carbon was sealed in a dryer and labelled as Sn/Sb-Mn-GAC for further use.

Following liquid chromatography conditions were used: Agilent chromatographic column ZORBAX SB-Aq (4.6×250 mm; 5 μm), mobile phase (volumetric ratio of 3:7) acetonitrile: 0.02 mol/L potassium dihydrogen phosphate solution (pH of 2.00), column temperature of 30.00°C, ultraviolet detector with the detection wavelength of 210 nm, injection volume was 20 μL and the flow rate was 1.000 mL/min. The mobile phase was filtered through a 0.45 μm membrane, and degassed using ultrasound. The samples were filtered through a 0.45 μm needle filter.

The drawing of standard curve: The concentration of 4-chlorophenol in electrolyte and the concentration of electrolytic intermediates were analyzed using high-performance liquid chromatography (1260; Agilent Technologies, Inc., USA). In addition, solutions with different concentrations were prepared for the HPLC analysis. The HPLC standard curves of the corresponding substances were plotted with the concentration of each substance plotted as abscissa and the peak area as ordinate. The results are presented in Table 1.

2.3 Structural characterization

The surface morphology of activated carbon was analyzed using the field emission scanning electron microscopy (SUPRA 55, Karl Zeiss, Germany). The elemental composition of the modified activated carbon was analyzed using an OXFORD X-
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2.4 Electrochemical tests

Chenhua CHI660E electrochemical workstation was used to study the electrochemical properties of the particle electrodes. During the tests, the self-made carbon paste electrode was used as the working electrode. The saturated calomel electrode was used as the reference electrode, whereas the platinum electrode was used as the auxiliary electrode. Besides, the preparation method of carbon paste electrode was as follows. First, an appropriate amount of particle electrode was ground into powder. Then, a certain amount of conductive carbon black was added into the particle electrode. The ratio of particle electrode to conductive carbon black was 8:1 in volume. Finally, the particle electrode powder and the conductive carbon black were mixed uniformly. The liquid paraffin was added to make the paste. Then, the paste mixture was filled into the carbon paste electrode. Within the range of 1–1.5 V, the linear voltammetric curves were successively measured in 0.15 mol/L Na2SO4 solution and 0.15 mol/L Na2SO4 + 500 mg/L 4-chlorophenol solution at the scanning speed of 20 mV/s.

Figure 1 shows the schematic of the experimental apparatus. The three-dimensional electrochemical experiments were conducted in a 480 cm³ (10 cm in length, 4.8 cm in width, and 10 cm in height) organic glass electrolytic cell. The DSA plate anode (8 cm in width, 14 cm in height, and 0.5 mm in thickness) and titanium plate cathode were placed perpendicular to the bottom of the electrolyzer. The depth of the 4-chlorophenol simulated wastewater in the electrolytic cell was approximately 4.5 cm and the area of single-sided electrode plate which was contacted to the simulated wastewater was approximately 36 cm² (8 cm in width, and approximately 4.5 cm in height). Both sides of the DSA plate anode and titanium plate cathode were exposed to the solution. Furthermore, the reactor was filled with a certain amount of Sn/Sb-Mn-GAC particle electrodes.

In the light of the experimental apparatus shown in Fig. 1, a three-dimensional electrochemical reactor was constructed using Sn/Sb-Mn-GAC particle electrodes. DC regulated power supply (PS-303D-II; Zhaoxin Electronic Instrument Co., Ltd., China) was used in the electrochemical degradation process. The 4-chlorophenol solution with a volume of 300 mL and a concentration of 500 mg/L was prepared as simulated wastewater. Then, the 4-chlorophenol solution was electrochemically treated with a certain concentration of Na2SO4, electrode plate distance, current intensity, and Sn/Sb-Mn-GAC particle electrode dosage. The data were collected every 5 minutes. The removal rate of 4-chlorophenol (%) was calculated using Eq. (7).

\[
y = \frac{C_0 - C_t}{C_0}
\]

where \(C_0\) is the initial concentration of 4-chlorophenol in the solution and \(C_t\) is the concentration of 4-chlorophenol at time \(t\).

3. Results and Discussion

3.1 Characterization of particle electrodes

3.1.1 Structural characterization

Figure 2(a) and 2(b) show the surface morphologies of activated carbon before and after loading Sn/Sb-Mn-GAC, respectively. It can be seen from Fig. 2(b) that the surface of Sn/Sb-Mn-GAC has nearly the same particle size and uniform distribution of particles on the surface of activated carbon. Furthermore, the surface particles are fine and uniform in size. On this account, when the particle electrode was used as a three-dimensional electrode, the specific surface area of the particle electrode increased significantly. Therefore, the contact area between the surface of the particle electrode and organic pollutants increased, which was beneficial in improving the efficiency of electrooxidation reaction.

Figure 3 shows the XRD spectra of particle electrodes. The diffraction peak of the original activated carbon matrix was not obvious, indicating that the GAC is amorphous. Additionally, the results were found to be consistent with the properties of GAC. Figure 3 shows that the Sn/Sb-Mn-GAC had a diffraction peak at the 2θ value of 26.7°, which was the characteristic diffraction peak of SnO2. However, there was no characteristic diffraction peak of Mn and Sb elements. This could be due to the amorphous structure of Mn and Sb oxides distributed on the surface of GAC.

| Substance                  | Standard curve | Correlation coefficient |
|----------------------------|---------------|------------------------|
| 4-chlorophenol (0.10–10.00 mg·L⁻¹) | \(Y = 40.0X + 2.9\) | \(R^2 = 0.9998\) |
| 4-chlorophenol (10.00–40.00 mg·L⁻¹) | \(Y = 39.1X + 66.3\) | \(R^2 = 0.9996\) |
| 4-chlorocatechol            | \(Y = 97.9X - 17.4\) | \(R^2 = 0.9996\) |
| p-benzoquinone             | \(Y = 18.8X - 5.5\)  | \(R^2 = 0.9991\) |
| hydroquinone               | \(Y = 46X + 0.79\)    | \(R^2 = 0.9996\) |
| fumaric acid               | \(Y = 130.4X - 1.9\)  | \(R^2 = 0.9998\) |
| oxalic acid                | \(Y = 18.36X + 5.5\)  | \(R^2 = 0.9992\) |

MaxN51-XMX1004 energy spectrometer that was equipped with the scanning electron microscopy.

The activated carbon was analyzed using the X-ray diffractometer (X’Pert PRO; Malvern Panalytical B.V., The Netherlands). The test conditions were as follows. Copper target (\(\lambda_Ka = 1.54006 \ \text{Å}\)), step length 0.026°, scanning range 5°–80°, retention time per step: 20.4 s, voltage: 40 V, current: 40 mA.

**Table 1.** Liquid standard curve of each substance.

**Figure 1.** Schematic of the experimental apparatus. (1) Anode plate (2) Cathode plate (3) Particle electrode (4) 4-chlorophenol simulated wastewater (5) Electrolytic cell (6) Anode electrode wire (7) Cathode electrode wire (8) DC stabilized voltage supply.
3.1.2 Electrochemical properties

The oxygen evolution reaction is the main side-reaction in the electrochemical reaction. Higher the oxygen evolution potential, more difficult is the occurrence of side-reactions in the system. Therefore, it should be selected to reduce the occurrence of oxygen evolution side-reactions and reduce the current of oxygen evolution side-reactions. Therefore, the current efficiency can be improved and the catalytic oxidation degradation of organic pollutants can be promoted.

3.2 Effect of single process parameters on the removal rate of 4-chlorophenol

3.2.1 Electrolyte (Na2SO4) concentration

The simulated wastewater containing 500 mg·L⁻¹ of 4-chlorophenol with a volume of 300 mL was electrolyzed for 90 minutes at a distance of 4 cm between the two electrode plates. The dosage of Sn/Sb-Mn-GAC particle electrode was 10 g, whereas the current was 1 A. Furthermore, the Na2SO4 concentration of varied through values of 1.5 g·L⁻¹, 2 g·L⁻¹, 3 g·L⁻¹, and 4 g·L⁻¹. The removal rate of 4-chlorophenol was investigated and the experimental results are shown in Fig. 5.

In the electrochemical reaction, it is necessary to add supporting electrolytes, such as Na2SO4, NaCl, K2SO4, and KCl to improve the conductivity of solution due to the weak conductivity of the organic solution. In this study, Na2SO4 was used as the electrolyte in 4-chlorophenol wastewater during the process of electrochemical treatment. Figure 5 shows that, with the increase in the Na2SO4 concentration in 4-chlorophenol wastewater, the removal rate of 4-chlorophenol first increased and then decreased. When the concentration of Na2SO4 was 2 g·L⁻¹, the removal rate of 4-
chlorophenol reached 99.12%, which was the highest value for the degradation rate. With the further increase in the concentration of electrolyte, the charge in the solution increased, thus strengthening the electrolysis process. However, the resistance of positive and negative charges will also increase for a very high concentration of the electrolyte. Therefore, the electrolysis efficiency will decrease. Based upon these results, the optimum Na₂SO₄ concentration of 2 g·L⁻¹ was selected.

3.2.2 Electrode plate distance

The simulated wastewater containing 500 mg·L⁻¹ of 4-chlorophenol with the total volume of 300 mL was electrolyzed for 90 minutes with the Na₂SO₄ concentration of 2 g·L⁻¹. The dosage of Sn/Sb-Mn-GAC particle electrode was 10 g, whereas the current was 1 A. Additionally, the distance between the two electrode plates was varied through values of 1 cm, 2 cm, 3 cm, and 4 cm. The removal rate of 4-chlorophenol was investigated and the experimental results are shown in Fig. 6.

Figure 6 shows that, with the increase in the distance between the electrode plates, the removal rate of 4-chlorophenol first increased and then decreased. The removal rate of 4-chlorophenol reached the value of 96.38%, which was the highest value at a distance of 2 cm between the two electrode plates. When the distance between the electrode plates was decreased, the rate of charge movement in the solution increased, which improved the current efficiency. However, when the distance between the electrode plates is too short, the number of available charges will be reduced between the electrode plate. Due to this reason, the electrolysis efficiency will reduce. Based upon these results, the distance of 2 cm was chosen as the optimum distance between the two electrode plates.

3.2.3 Current intensity

The simulated wastewater containing 500 mg·L⁻¹ of 4-chlorophenol with the total volume of 300 mL was electrolyzed for 90 minutes with the Na₂SO₄ concentration of 2 g·L⁻¹. The distance between the two electrode plates was 2 cm, whereas the dosage of Sn/Sb-Mn-GAC particle electrode was 10 g. Furthermore, the current intensity was varied through values of 0.5 A, 1 A, 1.5 A, and 2 A. The removal rate of 4-chlorophenol was investigated and the experimental results are shown in Fig. 7.

Figure 7 shows that, with the increase in the current intensity, the removal rate of 4-chlorophenol continuously increased. However, when the current intensity reached the value of 1.5 A, the removal rate of 4-chlorophenol became 99.18%, which was similar to the value observed for the current of 2 A. Based upon these results, 1.5 A of current intensity was chosen as the optimum current intensity.

3.2.4 Sn/Sb-Mn-GAC particle electrode dosage

The simulated wastewater containing 500 mg·L⁻¹ of 4-chlorophenol with the total volume of 300 mL was electrolyzed for 90 minutes with the Na₂SO₄ concentration of 2 g·L⁻¹. The distance between the two electrode plates was 2 cm, whereas the current intensity was 1.5 A. Furthermore, the dosage of Sn/Sb-Mn-GAC particle electrode was varied through values of 5 g, 10 g, 15 g, and 20 g. The removal rate of 4-chlorophenol was investigated and the experimental results are shown in Fig. 8.

Figure 8 shows that, with the increase in the particle electrode dosage, the removal rate of 4-chlorophenol obviously increased. Additionally, the reaction area of 4-chlorophenol also increased. Therefore, it was beneficial to increase the degradation of 4-chlorophenol by increasing the particle electrode dosage. However, when the particle electrode dosage reached the value of 15 g, the removal rate of 4-chlorophenol was nearly 100%, which was similar to the condition of particle electrode dosage of 20 g. Based upon these results, 15 g was chosen as the optimum dosage of particle electrode.

3.3 Response surface design and model analysis
3.3.1 Box-Behnken design experiments

On the basis of single factor experiments, Design-Expert was used to investigate the effects of Na₂SO₄ concentration, electrode plate distance, current intensity and particle electrode dosage on the removal rate of 4-chlorophenol. The removal rate of 4-chlorophenol
was the response value $Y$ after 60 minutes of electrolysis. Table 2 presents the 4-factor and 3-level Response Surface Experiment results. Table 3 presents the Box-Behnken design with Na$_2$SO$_4$ concentration, electrode plate distance, current intensity, and particle electrode dosage for 29 experimental trials.

### 3.3.2 Variance analysis of regression model

The quadratic polynomial regression equation was developed by applying the multivariate regression fitting methods on the experimental data for the removal rate of 4-chlorophenol (presented in Table 3). The quadratic polynomial is given by Eq. (8).

$$
Y = 90.77 + 0.42A - 0.21B + 9.64C + 8.99D - 0.44AB - 0.74AC + 0.84AD + 1.69BC - 2.51BD - 0.5CD - 0.73A^2 - 2.66B^2 - 4.68C^2 - 5.99D^2
$$

where $Y$ is the removal rate of 4-chlorophenol (%), $A$ is the Na$_2$SO$_4$ concentration (g·L$^{-1}$), $B$ is the electrode plate distance (cm), $C$ is the current intensity (A), and $D$ is the particle electrode dosage (g). Furthermore, the analysis of variance (ANOVA) for the quadratic polynomial regression model was conducted and the corresponding results are presented in Table 4.

The results presented in Table 4 show that the Model (Prob > F)-value of less than 0.0001 implies that the model is highly significant. In the linear item of the model, $C$ and $D$ are near to be significant ($P < 0.0001$). Besides, in the quadratic term of the model, $B^2$, $C^2$, and $D^2$ are also near to be significant. The lack of fit value is 5.29, which is not significant relative to the pure error, due to which, it is reasonable to choose the model to fit the data. By analyzing the variance of the model, the correlation coefficients $R^2$ is calculated to be 0.9598, which shows that the model can describe 95.98% of the data. In short, the regression equation can better describe the experimental results, and it is feasible to use the equation to simulate the experiments.

### 3.3.3 Analysis of the response surface curve

Figure 9 shows that a response surface graph of the interaction among various factors. It can be seen that the interaction among the factors in the response surface is not significant. Figure 9 shows that the effect of electrode plate distance and electrolyte concentration on the removal rate of 4-chlorophenol is the smallest. With the increase in the distance between the electrode plates, the removal rate of 4-chlorophenol first increases and then decreases, while the effect of

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**Table 2.** Response surface experimental factors and levels.

| Factor                  | Level | -1  | 0   | 1   |
|-------------------------|-------|-----|-----|-----|
| Na$_2$SO$_4$ concentration (g·L$^{-1}$) | 1.5   | 2   | 2.5 |
| electrode plate distance (cm)    | 1     | 2   | 3   |
| current intensity (A)        | 1     | 1.5 | 2   |
| particle electrode dosage (g) | 5     | 10  | 15  |

**Table 3.** Box-Behnken design with four factors and its measured values.

| Na$_2$SO$_4$ concentration (g·L$^{-1}$) | Electrode plate distance (cm) | Current intensity (A) | Particle electrode dosage (g) | 4-chlorophenol removal rate (%) |
|----------------------------------------|--------------------------------|-----------------------|-------------------------------|--------------------------------|
| 1                                      | 2.00                           | 2.00                  | 10.00                         | 89.15                          |
| 2                                      | 2.00                           | 2.00                  | 1.50                          | 10.00                         | 92.79                          |
| 3                                      | 2.00                           | 2.00                  | 1.50                          | 10.00                         | 89.06                          |
| 4                                      | 2.50                           | 3.00                  | 1.50                          | 10.00                         | 82.97                          |
| 5                                      | 2.00                           | 2.00                  | 1.50                          | 10.00                         | 90.52                          |
| 6                                      | 2.00                           | 2.00                  | 1.50                          | 10.00                         | 90.43                          |
| 7                                      | 2.50                           | 2.00                  | 2.00                          | 10.00                         | 96.71                          |
| 8                                      | 1.50                           | 1.00                  | 1.50                          | 10.00                         | 90.49                          |
| 9                                      | 2.50                           | 2.00                  | 1.50                          | 15.00                         | 96.2                           |
| 10                                     | 2.50                           | 1.00                  | 1.50                          | 10.00                         | 88.66                          |
| 11                                     | 2.00                           | 1.00                  | 1.00                          | 10.00                         | 75.15                          |
| 12                                     | 1.50                           | 2.00                  | 1.00                          | 10.00                         | 73.83                          |
| 13                                     | 2.50                           | 2.00                  | 1.50                          | 5.00                          | 73.03                          |
| 14                                     | 2.00                           | 2.00                  | 1.50                          | 10.00                         | 91.05                          |
| 15                                     | 1.50                           | 3.00                  | 1.50                          | 10.00                         | 86.56                          |
| 16                                     | 2.00                           | 2.00                  | 2.00                          | 5.00                          | 84.14                          |
| 17                                     | 2.50                           | 2.00                  | 1.00                          | 10.00                         | 78.48                          |
| 18                                     | 2.00                           | 3.00                  | 1.50                          | 15.00                         | 90.79                          |
| 19                                     | 2.00                           | 2.00                  | 1.00                          | 5.00                          | 62.41                          |
| 20                                     | 2.00                           | 3.00                  | 1.50                          | 5.00                          | 76.63                          |
| 21                                     | 1.50                           | 2.00                  | 1.50                          | 5.00                          | 72.66                          |
| 22                                     | 2.00                           | 1.00                  | 1.50                          | 15.00                         | 93.94                          |
| 23                                     | 2.00                           | 2.00                  | 1.00                          | 15.00                         | 76.64                          |
| 24                                     | 1.50                           | 2.00                  | 2.00                          | 10.00                         | 95.01                          |
| 25                                     | 2.00                           | 1.00                  | 1.50                          | 5.00                          | 69.72                          |
| 26                                     | 1.50                           | 2.00                  | 1.50                          | 15.00                         | 92.48                          |
| 27                                     | 2.00                           | 2.00                  | 2.00                          | 15.00                         | 96.37                          |
| 28                                     | 2.00                           | 3.00                  | 2.00                          | 10.00                         | 94.19                          |
| 29                                     | 2.00                           | 3.00                  | 1.00                          | 10.00                         | 73.41                          |
electrolyte concentration on the removal rate of 4-chlorophenol is very insignificant. Figure 9 shows that the particle electrode dosage and the current intensity have the greatest impact on the removal rate of 4-chlorophenol. Meanwhile, with the increase of the particle electrode dosage and current intensity, the removal rate of 4-chlorophenol increased. In this study, the optimum electrolytic

### Table 4. Analysis of variance for the regression model.

| Source | Sum of squares | df  | Mean square | F-value | Probability-(Prob > F) |
|--------|---------------|-----|-------------|---------|------------------------|
| Model  | 2462.28       | 14  | 175.88      | 23.85   | <0.0001 significant    |
| A      | 2.10          | 1   | 2.10        | 0.28    | 0.6019                 |
| B      | 0.55          | 1   | 0.55        | 0.074   | 0.7895                 |
| C      | 1114.58       | 1   | 1114.58     | 151.15  | <0.0001                |
| D      | 968.94        | 1   | 968.94      | 131.40  | <0.0001                |
| AB     | 0.77          | 1   | 0.77        | 0.11    | 0.7507                 |
| AC     | 2.18          | 1   | 2.18        | 0.30    | 0.5956                 |
| AD     | 2.81          | 1   | 2.81        | 0.38    | 0.5472                 |
| BC     | 11.49         | 1   | 11.49       | 1.56    | 0.2324                 |
| BD     | 25.30         | 1   | 25.30       | 3.43    | 0.0852                 |
| CD     | 1.00          | 1   | 1.00        | 0.14    | 0.7182                 |
| A²     | 3.50          | 1   | 3.50        | 0.47    | 0.5023                 |
| B²     | 45.95         | 1   | 45.95       | 6.23    | 0.0256                 |
| C²     | 142.25        | 1   | 142.25      | 19.29   | 0.0006                 |
| D²     | 232.96        | 1   | 232.96      | 31.59   | <0.0001                |
| Residual error | 103.24 | 14 | 7.37 |          |                      |
| Lack of fit       | 95.97        | 10  | 9.60        | 5.29    | 0.0613 Not significant |
| Pure error         | 7.26         | 4   | 1.82        |         |                       |
| Cor. total     | 2565.51      | 28  |             |         |                        |

**Figure 9.** Response curve of each factor’s interaction.
conditions were found to be as follows. The Na$_2$SO$_4$ concentration was 2.14 g L$^{-1}$, whereas the distance between the two electrode plates was 1.88 cm. The current intensity was 1.97 A, whereas the particle electrode dosage was 13.78 g. However, the operational feasibility of the actual experiment was considered and the factors were revised. The revised conditions were as follows. The Na$_2$SO$_4$ concentration was 2 g L$^{-1}$, while the distance between the two electrode plates was 2 cm. The current intensity was 2 A, and the particle electrode dosage was 14 g. Under these conditions, the maximum response value of 4-chlorophenol removal rate model was found to be 95.67%.

3.4 Verification experiment

The 4-chlorophenol simulated wastewater was electrolyzed under optimized conditions. The experiment was carried out according to the method described in Section 2.4. The experiment was repeated thrice and the average values were used for analysis. The result showed that the removal rate of 4-chlorophenol was 96.13% with the relative error of 0.48%, which was close to the value obtained from the fitting model. Therefore, the electrolytic removal rate of 4-chlorophenol can be better predicted when the process conditions of a three-dimensional electrode reactor constructed using Sn/Sb-Mn-GAC particle electrodes were optimized using the response surface methodology. The optimized conditions are feasible and have practical significance.

4. Conclusions

There is a characteristic diffraction peak of SnO$_2$ at 26.7° for the Sn/Sb-Mn-GAC. The results of SEM and electrochemical analysis show that the particles on the surface of Sn/Sb-Mn-GAC are evenly distributed, and have small and uniform particle size. Furthermore, the electrode has high oxygen evolution potential, which can effectively reduce the occurrence of side-reactions and improve the current efficiency in the electrolysis process.

Compared with the traditional two-dimensional electrode reactor, the three-dimensional electrode reactor can effectively improve the removal efficiency of pollutants in wastewater. This paper studied the treatment of 4-chlorophenol containing wastewater using a three-dimensional electrochemical reactor constructed using Sn/Sb-Mn-GAC particle electrodes. Using sodium sulfate as the electrolyte, the DSA plate as the anode and the titanium plate as the cathode, the single factor experiment was designed to study the effects of Na$_2$SO$_4$ concentration, electrode plate distance, current intensity, Sn/Sb-Mn-GAC particle electrodes dosage on the degradation of 4-chlorophenol simulated wastewater of the process. On the basis of single factor experiments, response surface methodology was designed to optimize the electrolysis conditions for the degradation of 4-chlorophenol. The experimental results were as follows. The Na$_2$SO$_4$ concentration was 2 g L$^{-1}$, whereas the distance between the two electrode plates was 2 cm. The current intensity was 2 A, and the particle electrode dosage was 14 g. For the electrolysis time of 60 min, the 4-chlorophenol removal rate was higher than 96%, which was consistent with the model value.

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