Electrolysis Conditions Optimization of 4-Chlorophenol Degradation with Pd/graphene Gas-diffusion Electrode by Response Surface Methodology

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In order to find the best electrolysis conditions for 4-Chlorophenol degradation, adopted response surface methodology (RSM) and central composite design (CCD) to investigate the current density, electrolyte concentration, initial pH and reaction time. A basic quadratic equation for the degradation efficiency of 4-chlorophenol was expressed as a function of individual variables. The results indicated that the linear effects and the quadratic effects of the individual variables (R^2 reached 0.8062 and 0.8230 and was close to 1) were statistically significant. The model provided the optimized conditions as follows: the initial pH was 7.00, electrolyte (Na_2SO_4) concentration was 0.02 mol/L, the current density was 23 mA/cm^2, and the reaction time was 120 min. The degradation efficiency of the cathodic compartment was more than 95.4%, while anodic compartment's degradation efficiency was 91.1%. Ultimately, 4-chlorophenol was efficiently degraded under the synergistic effect of reduction and oxidation in the present system.

1. INTRODUCTION

The increasing water contamination has raised serious environmental concerns. Chlorophenols (CPs) represent an important class among the top priority pollutants in water and be listed as a specific priority toxic pollutants group in the Clean Water Act by the US EPA [1, 2]. In particular, CPs bring serious ecological problems, such as be suspected carcinogen and mutagen effect on living organisms

due to their high toxicity, recalcitrance, bioaccumulation and persistence in the environment[3, 4]. Therefore, it is important to develop an effective method to degrade CPs.

Due to electrochemical methods have advantages such as compatible to environment, ease of control, and amenability to automation and high efficiency, they have attracted significant attention in the wastewater treatment field [5]. In recent year, indirect electro-oxidation methods have been used for wastewater treatment because it can produce HO· which has strong oxidative. Carbon materials such as carbon/polytetrafluoroethylene [6], graphite [7, 8], carbon felt [9, 10], reticulated vitreous carbon [11, 12] and graphene [13, 14] are adopted as electrode materials for the electrochemical production of HO· on the cathode. However, there will form many chlorinated aliphatic intermediates during the oxidation process when the aromatic rings of chlorinated organic pollutants are opened. Therefore, this paper uses a synergistic effect of electrochemical reduction and oxidation to decrease intermediates toxicity. However, the best electrolysis conditions are not easy to determine.

When "one at a time" variation of the treatment variables is used to obtain the best degradation condition of wastewater treatments, there are two hypotheses in this method. One is that every parameter do not interact each other and the other is that the response value is only decided by the single varied parameter. However, the response variable of wastewater treatment is determined by the different variables and their interaction of each other [15, 16]. Response surface methodology (RSM), an effective statistical techniques to optimize the desired response affected by many factors and the interactions, can be used to quantify the data from the appropriate experimental design by evaluating multiple parameters and the interaction between them and at the same time, it can save time and labor force [17, 18]. Central composite design (CCD), an experimental design method in RSM, was introduced by Box and Wilson in 1951 as an alternative to full-level factorial design [19] to fit a model by the least squares technique [20]. With CCD, more information can be obtained from fewer experiments, and the interactions among the factors can be revealed from the data [21].

Organic synthesized diaphragm, DSA anode (Ti/IrO$_2$/RuO$_2$) and self-made Pd/graphene gas-diffusion cathode were used to construct an electrochemical degradation device for the degradation of the wastewater containing 4-chlorophenol. Using RSM analyzed the best electrolysis conditions determined by current density, electrolyte concentration, initial pH and reaction time.

2. MATERIALS AND METHODS

2.1. Preparation of Pd/graphene gas-diffusion cathodes

Graphene oxide and palladium chloride were used to synthesize the Pd/graphene catalysts by a formaldehyde reduction method. And graphene oxide was prepared by modified Hummer protocol. Then the catalysts were fully characterized using Raman spectroscopy, Fourier transform infrared spectrometry, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and cyclic voltammetry. The Pd particles, averaging 5.4 nm in size, were highly dispersed in the graphene and had an amorphous structure. The Pd/graphene catalysts were available according to the reported

result [22]. The Pd/graphene gas-diffusion cathodes were prepared according to the reported procedure [23].

2.2. Procedures

Electrolysis was conducted in a terylene diaphragm cell of 100 mL, as reported by Wang [24]. The anode was a $Ti/IrO_2/RuO_2$ (Wuhan Kaida Technology Engineering Co., Ltd) net of 16 cm^2. The cathode was a Pd/graphene gas-diffusion electrode of 16 cm^2. A laboratory direct current power supplied with current-voltage monitor (GD1791 Guodian Ya Guang Power Technology (BJ) co., Ltd) was employed to provide the electric power. The synthetic wastewater was used. The current density, the concentration of supporting electrolyte (Na_2SO_4), the initial pH and the reaction time were determined by CCD. Before the experiment started, hydrogen gas was fed to the system for 5 min to insure dissolved gas saturation, and the rate of the feed gas was 25 mL/s. Hydrogen gas was fed into the gas compartment during the 0-60 min electrolysis. After 60 min of electrolysis, air was fed into the gas compartment. The electrolysis proceeded at room temperature. The high performance liquid chromatography (HPLC, Shimadzu, Japan) was used to determine 4-CP through the means of comparison of the retention times to it standard compounds. The samples (20 μL) were passed through 0.45 μm PTFE filters before given injection into the HPLC. The Znertisl ODS-SP C18 column (250 mm × 4.6 mm, 5 μm) would carry out the separation when flow rate was at 1.0 mL/min and temperature was 25°C. The determination of 4-CP was performed using HPLC with setting UV-detector at 280 nm and containing mobile phase methanol/water (v/v) 80/20.

2.3. Experimental design

Table 1. Range of different factors investigated with Central Composite Design

Factors	Code	Level				
		-2	-1	0	1	2
Current density (mA/cm^2)	X_1	15	20	25	30	35
Concentration (mol/L)	X_2	0.02	0.04	0.06	0.08	0.10
Initial pH	X_3	3	5	7	9	11
Reaction time（min）	X_4	40	60	80	100	120

As an empirical statistical method, except for being employed for multiple regression analysis, RSM can achieve the goals that solve multivariate equations at the same time by using the appropriate data from properly designed experiments [25, 26]. In this work, RSM was adopted to study the simultaneous effect of the electrolyte concentration, initial pH, current density and reaction time. The factors were selected as the independent variables, and the degradation efficiency of 4-chlorophenol was selected as the dependent variable. In order to describe the experimental conditions, we chose five levels of each variable. The arrangement of the CCD, as shown in Table 1, was designed to allow the development of the appropriate empirical equation 1[27, 28]:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4$$

$$\text{(1)}$$

Where x_1, x_2, x_3 and x_4 are the variables for the current density, electrolyte concentration, initial pH and reaction time, respectively. y represents the degradation efficiency of 4-chlorophenol. The predicted response (y) was therefore correlated to the set of regression coefficients (β): the intercept (β_0), linear (β_1, β_2, β_3, β_4), interaction (β_{12}, β_{13}, β_{14}, β_{23}, β_{24}, β_{34}) and quadratic coefficients (β_{11}, β_{22}, β_{33}, β_{44}). As a result, the total number of conditions in this design was calculated as 30 (=2^k+2k+6), where k is the number of factors (k=4). Design Expert software was used to analyze the experimental data and optimize the experimental conditions.

3. RESULTS AND DISCUSSION

3.1. Central composite design and data analysis

The complete CCD consisted of 30 and the responses of the degradation efficiency were synthesized in Table 2.

Table 2. Response values of Central Composite Design

	Code				Value				Efficiency（%）	
Run	X_1	X_2	X_3	X_4	X_1	X_2	X_3	X_4	Anode	Cathode
1	-1	-1	-1	-1	20	0.04	5	60	48.6	58.7
2	1	-1	-1	-1	30	0.04	5	60	72.6	77.5
3	-1	1	-1	-1	20	0.08	5	60	35.9	65.6
4	1	1	-1	-1	30	0.08	5	60	64	64.9
5	-1	-1	1	-1	20	0.04	9	60	54.5	57
6	1	-1	1	-1	30	0.04	9	60	74.8	75.6
7	-1	1	1	-1	20	0.08	9	60	65.8	67.5
8	1	1	1	-1	30	0.08	9	60	66.7	74
9	-1	-1	-1	1	20	0.04	5	100	56.4	59.4
10	1	-1	-1	1	30	0.04	5	100	90.5	88.2
11	-1	1	-1	1	20	0.08	5	100	79.6	83.1
12	1	1	-1	1	30	0.08	5	100	83	84.9
13	-1	-1	1	1	20	0.04	9	100	74.5	76.3
14	1	-1	1	1	30	0.04	9	100	90.4	86.3
15	-1	1	1	1	20	0.08	9	100	60.3	63.3
16	1	1	1	1	30	0.08	9	100	73.8	75.6

17	-2	0	0	0	15	0.06	7	80	26.8	30.9
18	2	0	0	0	35	0.06	7	80	52.6	59.6
19	0	-2	0	0	25	0.02	7	80	86.7	89.3
20	0	2	0	0	25	0.10	7	80	66.7	77.8
21	0	0	-2	0	25	0.06	3	80	72.2	77.8
22	0	0	2	0	25	0.06	11	80	44	59
23	0	0	0	-2	25	0.06	7	40	43.1	46.3
24	0	0	0	2	25	0.06	7	120	81.9	83.8
25	0	0	0	0	25	0.06	7	80	84.4	82.3
26	0	0	0	0	25	0.06	7	80	84.4	82.3
27	0	0	0	0	25	0.06	7	80	84.4	82.3
28	0	0	0	0	25	0.06	7	80	84.4	82.3
29	0	0	0	0	25	0.06	7	80	84.4	82.3
30	0	0	0	0	25	0.06	7	80	84.4	82.3

Further, the analyses of variance (ANOVA) of the quadratic regression model of the degradation efficiency in the anodic compartment and in the cathodic compartment were shown in Table 3 and Table 4.

Table 3. ANOVA in the anodic compartment

Source	Sum of Squares	Degree of freedom	Mean Square	F-value	P-value	Significance
Model	6273.81	14	448.3	4.46	0.0034	Significant
A	88.17	1	88.17	0.88	0.3639	
B	107.53	1	107.53	1.07	0.3175	
C	1195.68	1	1195.68	11.89	0.0036	
D	1450.81	1	1450.81	14.43	0.0017	
AB	8.70	1	8.70	0.087	0.7727	
AC	151.29	1	151.29	1.50	0.2389	
AD	264.06	1	264.06	2.63	0.1260	
BC	42.25	1	42.25	0.42	0.5267	
BD	24.50	1	24.50	0.24	0.6287	
CD	33.64	1	33.64	0.33	0.5716	
A^2	497.37	1	497.37	4.95	0.0419	
B^2	1.49	1	1.49	0.015	0.9046	
C^2	2466.75	1	2466.75	24.53	0.0002	
D^2	390.01	1	390.01	3.88	0.0677	
Residual	1508.55		1508.55			
Lack of Fit	1386.74	10	100.57	5.69	0.0343	Significant
Pure Error	121.81	5	138.67			
Cor Total	7782.36	29	24.36			

Table 2 and Table 3 shown that the results were fitted with one basic quadratic equation. The date of regression coefficients were computed, the response variables and the test variables in the anodic compartment were related by quadratic equation 2:

$$y_1=84.40+7.99x_1-3.05x_2-1.09x_3+8.47x_4-9.68\,x_1^2\,-0.43\,x_2^2\,-5.08\,x_3^2\,-3.98\,x_4^2\,-3.02x_1x_2-2.44x_1x_3-0.40x_1x_4-1.37x_2x_3+0.19x_2x_4-3.20x_3x_4 \qquad (2)$$

Where x_1, x_2, x_3 and x_4 are the variables for the current density, electrolyte concentration, initial pH and reaction time, respectively. y_1 represents the degradation efficiency of 4-chlorophenol in the anodic compartment. The ANOVA analysis by multiple regression using P-value was performed for determination of the constants, coefficients of linear, quadratic and interaction effects. The P-value greater than 0.1 indicates that the model terms were not significant, while this value less than 0.05 indicated significant model terms. The small P-value (0.0034) and large F-value (4.46) implied that the quadratic model was significant [29, 30]. The lack-of-fit F-value of 5.69 implied that it was significant. Compare with conclusions of other studies, the adequate precision measures of the signal to noise ratio and a value greater than 4 was desirable [31, 32]. The ratio of 8.251 indicated an adequate signal. Hence, the model can be used to navigate the design space. The ANOVA indicated that the linear coefficients, quadratic coefficients and interaction coefficient were significant, with small p-values. The equation regression coefficient value indicated that this equation was valid.

Table 4. ANOVA in the cathodic compartment

Source	Sum of Squares	Degree of freedom	Mean Square	F-value	P-value	Significance
Model	6273.8	14	306.36	5.00	0.0019	significant
A	117.93	1	117.93	1.92	0.1858	
B	10.14	1	10.14	10.14	0.6900	
C	871.2	1	871.2	14.21	0.0019	
D	902.83	1	902.83	14.72	0.0016	
AB	20.7	1	8.70	0.34	0.5698	
AC	9.61	1	20.7	0.16	0.6978	
AD	87.42	1	9.61	1.43	0.251	
BC	128.82	1	87.42	2.1	0.1678	
BD	0	1	128.82	0	1	
CD	0.72	1	0	0.012	0.915	
A$_2$	137.57	1	0.72	2.24	0.1549	
B$_2$	57.5	1	137.57	0.94	0.3482	
C$_2$	1767.33	1	57.5	28.82	< 0.0001	
D$_2$	259.71	1	1767.33	4.24	0.0574	
Residual	919.74	15	259.71			
Lack of Fit	902.76	10	61.32	26.59	0.0010	significant
Pure Error	16.97	5	90.28			
Cor Total	5208.76	29	3.39			

Table 2 and Table 4 shown that the results were fitted with one basic quadratic equation. The date of regression coefficients were computed, the response variable and the test variables in the cathodic compartment were related by quadratic equation 3:

$$y_2 = 82.30 + 6.40x_1 - 0.96x_2 - 1.85x_3 + 6.30x_4 - 8.13\ x_1^2 + 1.45\ x_2^2 - 2.34\ x_3^2 - 3.18\ x_4^2 - 3.52x_1x_2 - 0.08x_1x_3 + 0.61x_1x_4 - 1.84x_2x_3 - 0.41x_2x_4 - 1.34x_3x_4 \quad (3)$$

Where x_1, x_2, x_3 and x_4 are the current density, electrolyte concentration, initial pH, and reaction time, respectively. y_2 stands for the cathodic compartment's degradation efficiency of 4-chlorophenol. Determination of the constants, coefficients of linear, quadratic and interaction effects were performed by the ANOVA multiple regression analysis using P-value. When P-value was greater than 0.1, it indicated the model terms were not significant. However P-value was less than 0.05, significant model terms were achieved. Based on the small P-value (0.0019) and large F-value (5.00), we concluded that the quadratic model was fit to the actual results [29, 30]. The lack-of-fit F-value of 26.59 exhibited the mode was acceptable. And the adequate precision measures for the signal to noise ratio was performed and the ratio of 9.448 was achieved. Therefore, the chosen model was suitable for the design space. The ANOVA with small P-values showed that the linear coefficients, quadratic coefficients and interaction coefficient were acceptable. And the equation could be used to predict the cathodic compartment's degradation efficiency.

3.2. Comparison of the experimental values and the predicted values

The comparison of the experimental values and the predicted values of the degradation efficiency is shown in Figure 1.
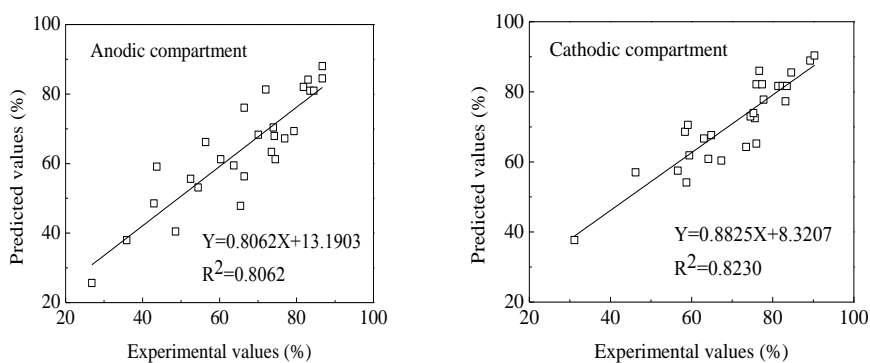

Figure 1. Comparison between the experimental and predicted values of the degradation efficiency

The results show the experimental and predicted values of the 4-chlorophenol degradation efficiency had good correlation; the correlation coefficients of the anodic and cathodic compartment were 0.8062 and 0.8230, respectively, and conformed to the equations $Y = 0.8062X + 13.1903$ and $Y = 0.8825X + 8.3207$, respectively. The R^2 of the anodic and cathodic compartments reached 0.8062 and 0.8230 and closed to 1, indicating a good linear correlation. These results show that using response surface methodology to predict the experimental data had good results.

As shown in Figure 2, the standard deviation of the experimental and predicted values of 4-chlorophenol degradation efficiency was small at 7.2; the correlation coefficient was 0.8980 and had good consistency, indicating that the response surface methodology was valid.
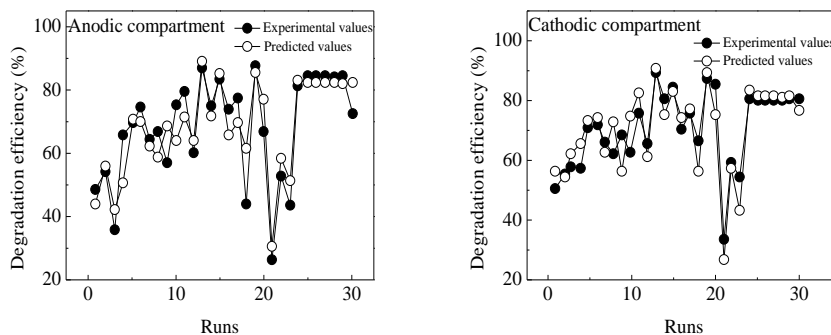

Figure 2. Comparison between the experimental and predicted values of the degradation efficiency

3.3. Efficiency of the initial pH and electrolyte concentration to degrade 4-chlorophenol

When the current density was 25 mA/cm^2, the results of the efficiency of the initial pH and electrolyte concentration in the anodic and cathodic compartments to degrade 4-chlorophenol is shown in Figure 3.
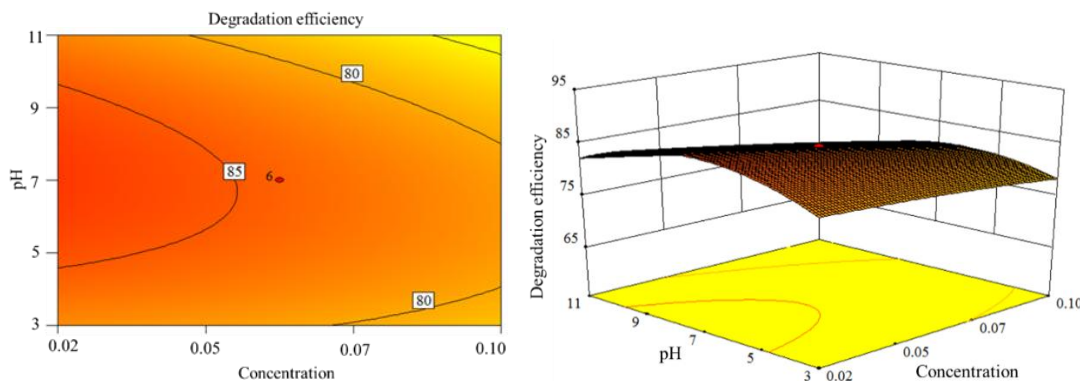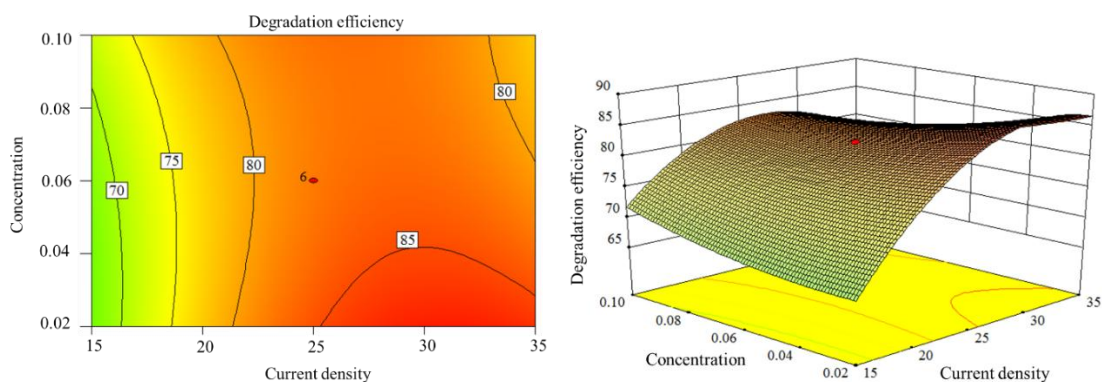

Figure 3. Surface plots for the effect of pH and electrolyte concentration on 4-chlorophenol degradation efficiency

Figure 3 shows the efficiency of the initial pH and electrolyte concentrations to degrade 4-chlorophenol in the cathodic and anodic compartments when the current density was 25 mA/cm^2. Within the range of the selected factors, the initial pH and electrolyte concentration had a significant interaction; the degradation efficiency of 4-chlorophenol increased with increasing initial pH in the cathodic and anodic compartments until the pH rose to 7.00. An acidic or alkaline environment prevented the reaction. When the concentration of Na_2SO_4 rose from a low level to a high level, the degradation efficiency of 4-chlorophenol decreased. Finally, 4-chlorophenol was efficiently degraded by the coefficient effects of reduction and oxidation in the system. In the system, the electrolyte Na_2SO_4 as a conductive medium did not participate in the electrochemical reaction. When the

concentration of Na_2SO_4 is high, the electrode surface generates a layer of salt membrane and prevented the electrode functioning normally. From the analysis, when the current density was 0.02 mol/L, the initial pH was 7.00, and the concentration of Na_2SO_4 was 0.02 mol/L, the efficiency of 4-chlorophenol degradation was relatively high.

3.4. Efficiency of the electrolyte concentration and current density to degrade 4-chlorophenol

When the initial pH was 7.00, the results of the efficiency of the electrolyte concentration and current density in anodic and cathodic compartments to degrade 4-chlorophenol is shown in Figure 4.

Figure 4. Surface and contour plots for the effect of the current density on the 4-chlorophenol degradation efficiency

Figure 4 shows the efficiency of the current density and electrolyte concentration to degrade 4-chlorophenol in the cathodic and anodic compartments when the initial pH was under the condition of the central value. When the current density rose, a greater number of electrons were supplied to the reaction, the reaction rate was faster and the degradation efficiency of 4-chlorophenol increased gradually in the cathodic and anodic compartments. When the current density was 23 mA/cm^2, the degradation efficiency was the highest. When the current density was higher than 23 mA/cm^2, the degradation efficiency decreased because side reactions significantly increased. When the electrolyte concentration was 0.02 mol/L, the degradation efficiency was the highest. From the analysis, when the initial pH was 7.00, the current density was 23 mA/cm^2 and the electrolyte concentration was 0.02 mol/L, the degradation efficiency was relatively high.

3.5. Efficiency of the initial pH and current density to degrade 4-chlorophenol

When the electrolyte concentration was 0.02 mol/L, the results of the efficiency of the initial pH and current density in the anodic and cathodic compartments to degrade 4-chlorophenol is shown in Figure 5.
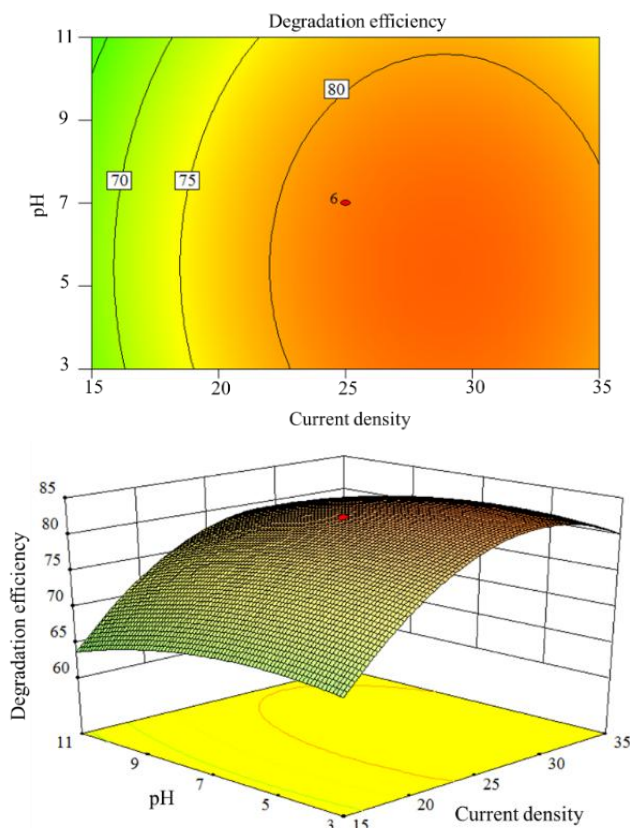
Figure 5. Surface and contour plots for the effect of the current density and initial pH on the 4-chlorophenol removal efficiency

Figure 5 shows the efficiency of the initial pH and current density to degrade 4-chlorophenol in the cathodic compartment when the electrolyte concentration was 0.02 mol/L. When the current density was less than 23 mA/cm^2, the degradation efficiency of 4-chlorophenol was not significant, and the efficiency rose with the increasing current density. When the current density was less than 23 mA/cm^2, due to the greater number of electrons supplied to the reaction, the reaction rate was faster. When the current density was 23 mA/cm^2, the degradation efficiency of 4-chlorophenol was the highest. When the current density was at a fixed value, the degradation efficiency of 4-chlorophenol increased with increasing initial pH. If the concentration was 7.00 and continued to rise, the degradation efficiency decreased. From the analysis, the degradation efficiency of 4-chlorophenol was best when the current density was 23 mA/cm^2 and the initial pH was 7.00.

In summary, using Design Expert software to analyze the data, combined with the response surface results, we concluded the best conditions for the greatest efficiency to degrade 4-chlorophenol in the cathodic and anodic compartments: the initial pH was 7.00, electrolyte (Na$_2$SO$_4$) concentration was 0.02 mol/L, the current density was 23 mA/cm^2, and the reaction time was 120 min. The degradation efficiency of the cathodic and anodic compartments was more than 95.4% and 91.1%, respectively.

4. CONCLUSIONS

RSM was applied to optimize the electrolysis conditions of 4-chlorophenol degradation. The reaction conditions such as current density, concentration of supporting electrolyte (Na_2SO_4), initial pH and reaction time were determined by CCD. A basic quadratic equation for the degradation efficiency of 4-chlorophenol was expressed as a function of the individual variables. The linear effects and the quadratic effects of the individual variables were statistically significant. The comparison of the experimental values and the predicted values of the degradation efficiency showed that RSM was valid and able to predict the experimental data. The obtained model gave the optimized conditions as follows: the initial pH was 7.00, electrolyte (Na_2SO_4) concentration was 0.02 mol/L, the current density was 23 mA/cm^2, and the reaction time was 120 min. The degradation efficiency of the cathodic and anodic compartments was more than 95.4% and 91.1%, respectively.

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