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UDC 66.087.5

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OPTIMIZATION OF CHROMIUM (VI) REMOVAL USING ELECTROCOAGULATION WITH IRON ELECTRODES

The electrocoagulation process can be modeled using an experimental design by conducting a few possible experiments, determining the relationship between factors, and their interrelationships, and determining the optimal conditions. In full factorial design analysis, the influence of factors such as pH, current density, and initial concentration was studied on the removal of Cr(VI) from an aqueous solution by electrocoagulation with iron electrodes. The removal efficiency of Cr(VI) was determined to be above 90% in this study at room temperature, pH 2.7-5.2, current density greater than 12 mA/cm^2, and relatively low initial concentrations.

Key words: *full factorial design, optimal condition, coagulant, removal efficiency.*

Introduction

Electrocoagulation is used to remove of various inorganic [1; 2; 3] and organic [4; 5] pollutants. The common removal methods for the of Cr(VI) from aqueous media are direct chemical precipitation, adsorption, ion exchange, membrane filtration, reverse osmosis, and electrocoagulation. Among these treatment methods, electrocoagulation is prominent with no additional chemicals, easy to automate and operate, minimal sludge production, and inexpensive [1].

During the electrocoagulation of the removal of Cr(VI) from an aqueous media, the redox reaction, chemical precipitation, and adsorption processes simultaneously take place. For this reason, the Cr(VI) removal process will be complex and depends on the only factor such as solution pH, current density, electrolyte concentration, initial concentration, and distance between electrodes and/or interrelation of these factors. Typically, on water and wastewater treatment by electrocoagulation, optimization has been performed by a single factor experiment keeping all other factors constant [6; 7]. This traditional optimization method requires many experimental runs and results in poor optimization, underestimation, or overestimation of the effects of the experimental variables due to disregarding the interactions among those variables. In addition, the single factor experimental design is time-consuming and requires many reagents to determine the optimized conditions. To overcome these disadvantages, the experimental design method has been used to determine the optimal condition and to display the effects of the main factors and their interrelations.

Since the 1990s, experimental design has become one of the most popular statistical techniques [8]. The advantages of experimental design are planning a few experiments, predicting experimental results, assuming the interdependence of factors, and obtaining precise results at minimum expense. The experimental design method determined the optimal conditions for removing organic [14; 15] and inorganic [16; 17] contaminants in an aqueous solution by electrocoagulation.

Tugba O. found that the optimal condition of electrocoagulation for the removal of Cr(VI) with iron electrodes was the current density of 0.39 mA/cm^2, electrolyte concentration of 33.6 mM NaCl, and experimental duration of 70 minutes from metal finishing wastewater using response surface methodology [18]. Contrastingly, Nahid M.G. et al. considered the effect of different factors such as the solution pH, current density, and Cr(VI) initial concentration, but chose the same method as Tugba et al. [19]. This research showed that the Cr(VI) removal efficiency was 100 % from tannery wastewater at 13 mA/cm^2, pH of solution 7, and Cr(VI) initial concentration of 750 mg/L. In these researches, although the experimental results are consistent with the uncertainties, such as the fact that the factors obtained vary, the current density is determined differently. The optimal condition of removal Cr(VI) by electrocoagulation was determined that the pH of the solution was 2.4 [15], 4.0 [7], and 7 [14], and the current density was 4.31 mA/cm^2 [7], 13 mA/cm^2 [14] and 20 mA/cm^2 [15] using the traditional single-factor experimental design method. This result was very different.

In addition to the response surface methodology, there are full or partial factorial design, central composite design, D-optimal design, and Box-Behnken design methods using experimental design [16].

The full factorial design simplifying the process and making research cheaper allow for many levels of analysis. As well as highlighting the relationships between factors, it also allows the effects of manipulating a single factor to be isolated and analyzed singly. This study was conducted in order to determine the optimal condition of the removal Cr(VI) by electrocoagulation from an aqueous solution using full factorial design analysis and to explain the correlation and factor relationship between the calculation and test results.

Materials and methods

Electrocoagulation experiment

A stock solution of Cr (VI) was prepared (1000 mg/L) by dissolving the required amount of potassium dichromate salt, $K_2Cr_2O_7$, and used for further experiments. 0.5 g NaCl was added to the chromium solution to increase the conductivity. The pH was adjusted to 3, 5, and 9 using 1.000 M NaOH or 1.000 M HCl and measured pH/ORP-meter (Hanna 2211). The iron electrodes were rubbed with sandpaper, washed with dilute HNO_3, distilled water 2-3 times before the electrocoagulation, and dried at 105°C (LabTech, LDO-250F). The electrocoagulation experiments were conducted using a

500 ml glass beaker with iron electrodes (3.9 cm×3.8 cm×0.2 cm). The volume of treated water in each experiment was 300 mL. The electrodes were attached to the power supply (BK-Precision 9110) with the galvanostatic condition. The distance between the anode and cathode was 1 cm. Water samples collected from the glass beaker were filtered at 0.45 micrometer filter paper before analysis. The determination of Cr(VI) was based on a 1, 5-dipenylcarbohydrazide spectrophotometric method. The absorbance was measured using n UV-Vis spectrophotometer (UV-Vis, Cary 1100) at 540 nm. The Cr(VI) removal (R, %) was calculated using the following formula:

$$R,\% = \frac{C_0 - C}{C_0} \times 100\% \qquad (1)$$

C_0 and C (mg/L) denote the Cr(VI) concentration before and after the electrocoagulation process, respectively.

Experimental design

The electrocoagulation depends on factors including the pH of the solution, initial concentration, current density, and distance between the electrodes. By establishing the relationship and optimal values between these factors, it is possible to carry out the electrocoagulation in a short period with high removal efficiency. The type of pH of the solution (x_1), current density (x_2), and initial Cr(VI) concentration (x_3) were selected as the factors with the low, intermediate, and high levels shown in Table.1. When the factors are quantitative in the 3^3 systems of designs, we often denoted the low, intermediate, and high levels by -1, 0, and +1, respectively. The data from the experiments are used to evaluate the applicable range of these factors, and they are used to deduce an experimental design using full factorial analysis.

Table 1

Ranges of selected experimental factors and their variation levels

Factor	Code	Level		
		-1	0	+1
pH of solution	x_1	3	5	9
Current density, mA/cm^2	x_2	10	20	30
Initial Cr(VI) concentration, mg/L	x_3	100	200	500

The full factorial analysis is a technique often used to describe the behavior of experimental data by generating a second or third order polynomial equation fitted to correlate the relationship between independent factors and responses, which accounts for variations caused by a linear, quadratic, and interactive effect of the process factors [20]. The statistical analysis of the results obtained in the electrocoagulation experiments was carried out in the PTC MathCad Prime 5.0 software. The model fitting was expressed by R-square (R^2), and the statistical significance of the model obtained and factors involved in the model were examined using P-value at a 95 % confidence level.

Experimental result

Both the experimental and predicted Cr(VI) removal efficiency for all 27 experiments are reported in Table 2. As can be seen from Table. 2 the predicted results were often higher than the experimental results.

Table 2

Experimental design and the experimental and predicted responses

№	x_1: pH of solution	x_2: current density	x_3: initial Cr(VI) concentration	Cr(VI) removal, %		
				Experimental	Predicted	Difference
1	3	30	500	91.69	102.91	+11.22
2	3	30	100	99.34	101.07	+1.73
3	3	30	200	98.99	108.20	+9.21
4	3	20	500	91.51	92.32	+0.81
5	3	20	100	99.32	101.75	+2.43
6	3	20	200	99.17	99.66	+0.49
7	3	10	500	59.04	62.16	+3.12
8	3	10	100	99.16	100.93	+1.77
9	3	10	200	83.49	85.10	+1.61
10	5	30	500	86.26	90.51	+4.25
11	5	30	100	99.38	105.68	+6.30
12	5	30	200	99.42	108.31	+8.89
13	5	20	500	65.50	81.17	+15.67
14	5	20	100	99.37	104.73	+5.36
15	5	20	200	99.32	98.85	-0.47
16	5	10	500	49.17	49.45	+0.28
17	5	10	100	99.32	99.46	+0.14
18	5	10	200	80.09	80.57	+0.48
19	9	30	500	76.86	94.84	+17.98
20	9	30	100	97.67	105.65	+7.98
21	9	30	200	99.39	108.85	+9.46
22	9	20	500	86.22	92.08	+5.86
23	9	20	100	97.65	105.50	+7.85
24	9	20	200	99.27	101.65	+2.38
25	9	10	500	55.29	61.33	+6.04
26	9	10	100	97.63	95.43	-2.20
27	9	10	200	72.45	80.01	+7.56

Experimental data are fitted with the third-order polynomial equation, where R is the Cr(VI) removal efficiency. The 'fullfact' and 'polyfitc' functions of the PTC MathCad Prime 5.0 software was utilized in the polynomial fitting.

$$\begin{aligned} R,\% = {} & -13.915 + 49.575 \times pH + 8.273 \times i - 0.099 \times C_0 + 0.604 \times pH \times i - 0.045 \\ & \times pH \times C_0 + 0.028 \times i \times C_0 - 10.136 \times pH^2 - 0.624 \times i^2 - 8.571 \\ & \cdot 10^{-4} C_0^2 - 3.607 \cdot 10^{-4} \times pH \times i \times C_0 - 0.017 \times pH^2 \times i + 0.004 \times pH^2 \\ & \times C_0 - 0.007 \times pH \times i^2 + 4.254 \cdot 10^{-6} \times pH \times C_0^2 - 2.258 \cdot 10^{-4} \times i^2 \times C_0 \\ & - 2.135 \cdot 10^{-5} \times C_0^2 \times i + 0.58 \times pH^3 + 0.011 \times i^3 + 1.578 \cdot 10^{-6} C_0^3 \end{aligned}$$

As can be seen from the results of the calculated third-order polynomial equations following relations:

1. *From linear relationship coefficients*: From the polynomial equation, the Cr(VI) removal efficiency is very influenced by the pH of the solution (+49.575), which has a positive main effect on the predicted value. The next influencing factor on the Cr(VI) removal efficiency is the current density with a

positive main effect 8.273 times. However, the initial concentration (-0.099) effect was relatively weak and had a negative relation to the removal of Cr(VI).

2. *From quadratic and cubic relationship coefficients*: The Cr(VI) removal efficiency was dependent on the following factors, strongly negative from the square of pH (-10.136 and 0.58). The current density (-0.624) and the initial concentration (8.571×10^{-4}) effect on the removal of Cr(VI) was weak and negative. However, the effect of the cubic member of initial concentration (1.578×10^{-6}). Since the initial Cr(VI) concentration is higher than the current density and pH of the solution, this cubic effect indicates a design flaw due to the sharp increase in Cr(VI) removal efficiency.

3. *From interaction coefficients between two and three factors:* The Cr(VI) removal efficiency was relatively weak correlation on the interaction effects of the two and three factors (pH of the solution, current density, and concentration). The contribution of the interaction effects of the two and three factors (pH of the solution, current density, and initial concentration) on the Cr(VI) removal efficiency was low.

It was observed that removal efficiencies increased with an increase in the values of the operating parameters having a positive sign for the coefficient, and a decrease with a decrease in the values of the operating parameters having a negative sign for the coefficients.

As shown here, the Cr(VI) removal efficiency was strongly dependent on the pH of the solution as regards the third-order polynomial equation. For example, when the initial concentration of Cr(VI) and the current density were constant at 200 mg/L, 18 mA/cm^2 and the pH of the solution was 2, the Cr(VI) removal efficiency was 88.48 %. However, when the pH of the solution was increased to 11, the removal efficiency increased by 1.8 times.

It is necessary to test the consistency between the accuracy of the third-order polynomial model and the experimental results [21]. The main effects of the three-factor (pH of the solution, current density, and Cr(VI) concentration) on the Cr(VI) removal efficiency for experimental and predicted results are shown in Figure 1.

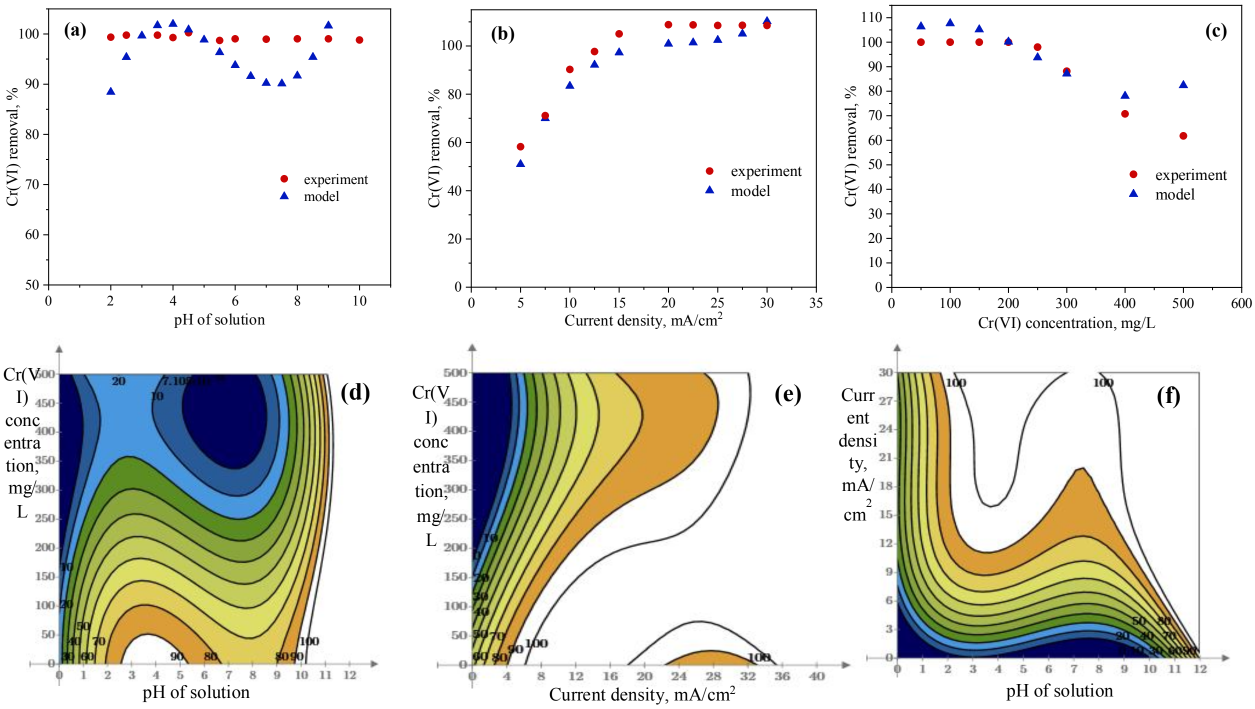

Figure 1. The relationship between the Cr(VI) removal efficiency and experimental parameters:

a) pH of the solution; b) current density; c) Cr(VI) concentration; d-f) the predicted contour plots of three factors

As can be seen from Figure 1a, a wide range of pH values, the predicted results differ from the experimental results due to the high values of linear and cubic coefficients of the third-order polynomial model equation. Particularly, a linear relation coefficient had a major effect on removal efficiency and reduced accuracy when the pH of the solution was between 2-3. However, the initial pH of the solution from 3 to 5 corresponds to the experimental result and predicted result. When the pH>9, the C(VI) removal efficiency was sharply increased in connection with the cubic relation coefficient of the polynomial equation.

From Figures 1b and c, the Cr(VI) removal efficiency for predicted results almost agreed with the experimental result for current density (5-30 mA/cm^2) and concentration (50-400 mg/L). As the current density increased from 30 mA/cm^2, the predicted values of the Cr(VI) removal efficiency deviated from the experimental values depending on the cubic member of the current density of the third-order polynomial equation. The Cr(VI) removal efficiency of the predicted value increased with increasing the concentration of Cr(VI). It is involved with the cubic member of concentration of the polynomial equation that positively affects on the Cr(VI) removal efficiency. This pattern can be seen in the contour map of the factor relationship (Figure 1d-f). The Cr(VI) removal efficiency is higher than 90 % when the pH of the solution is higher than 10, or the pH of the solution is between 2.7-5.2 and the initial concentration is lower than 50 mg/L (Figure 1d). When the current density was higher than 18 mA/cm^2, the Cr(VI) removal efficiency was 100%, regardless of the Cr(VI) initial concentration and pH of the solution (Figure 1e, f). As can be seen that the relationship between the Cr(VI) removal efficiency and the pH of the solution was strong and the relationship of the initial concentration was weak. The Cr(VI) removal efficiency was decreased when increasing the initial concentration, which is involved that the coagulants interacting with the Cr(VI) ions in the solution will not be formed enough. The polynomial equation is well suited to the experimental results in the low range of current density and the low range of the concentration and pH is between 3-5. Consequently, the pH of the solution is a major factor that influences Cr(VI) removal, but it directly depends on current density.

The full factorial design analysis results show that the optimal condition of electrocoagulation was pH of the solution 2.7-5.2, I>12 mA/cm^2, in the low range of Cr(VI) concentration at room temperature. The removal efficiency was more than 90% at this calculated condition, whichis consistent with our previous experimental results of pH 4.5, the current density of 15 mA/cm^2, and the initial solution concentration of 200 mg/L. [21]. The comparison of experimental and predicted values of Cr(VI) removal efficiency is presented in Figure 2. The agreement between the experimental and predicted values of Cr(VI) removal efficiency is satisfactory.

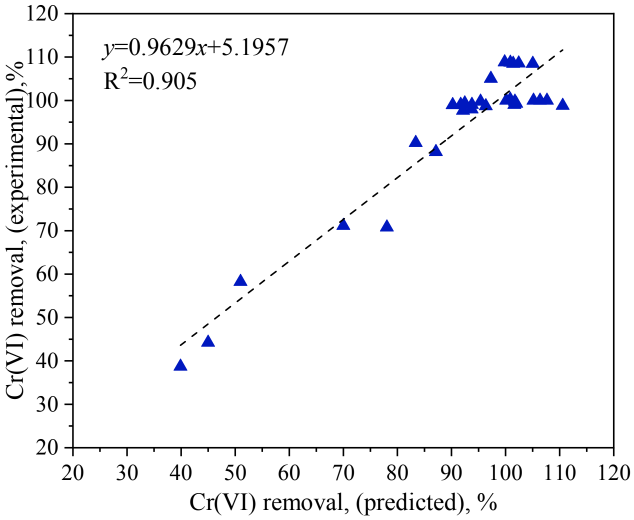

Figure 2. Comparison between experimental and predicted values for Cr(VI) removal

Conclusions

This study investigated the removal of Cr(VI) by electrocoagulation using iron sacrificial electrodes. Full factorial experimental 3^3 systems of designs have been applied to determine the optimal experimental conditions and performed only 27 experiments. The cubic-order polynomial equation referred to the Cr(VI) removal efficiency depends on the pH of the solution, current density, and initial concentration. The predicted results were consistent with the experimental results. However, the cubic-order polynomial equation was limited by the influence of the cubic coefficients at the high initial concentration and pH of the solution.

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ОПТИМИЗАЦИЯ УДАЛЕНИЯ ХРОМА (VI) С ПОМОЩЬЮ ЭЛЕКТРОКОАГУЛЯЦИИ ЖЕЛЕЗНЫМИ ЭЛЕКТРОДАМИ

Процесс электрокоагуляции может быть смоделирован с использованием экспериментального проекта путем проведения нескольких возможных экспериментов, определения взаимосвязи между факторами и их взаимосвязей, а также определения оптимальных условий. В ходе полного факторного анализа конструкции было изучено влияние таких факторов, как pH, плотность тока и начальная концентрация, на удаление Cr (VI) из водного раствора путем электрокоагуляции железными электродами. В этом исследовании было определено, что эффективность удаления Cr(VI) превышает 90 % при комнатной температуре, pH 2,7-5,2, плотности тока более 12 мА/см2 и относительно низких начальных концентрациях.

Ключевые слова: *полное факторное проектирование, оптимальное условие, коагулянт, эффективность удаления.*