Pitting corrosion of chloride ions in electrocoagulation for Cr(VI) removal: optimization by response surface methodology

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Abstract. This work observed an interesting phenomenon of pitting corrosion by chloride ions (Cl- ) in electrocoagulation (EC) for Cr(VI) removal. High Cr(VI) removal capacity was achieved by initiating pitting corrosion on iron surface with Cl- over 50 mg L\(^{-1}\), as showed by environmental scanning electron microscope analysis (ESEM). Then response surface methodology (RSM) was applied to optimize the Cr(VI) removal in the case of Cl-. RSM suggested that the optimal operation conditions were initial pH at 5.24, applied currents at 0.914 A and Cl- concentration at 54.37 mg L\(^{-1}\). The verification test showed 99.98 % of Cr(VI) removal efficiency under the above optimal condition. Our study indicated that Cl- can act as an enhancement factor by pitting corrosion in EC for Cr(VI) removal.

1. Introduction
Chromium (Cr), as a common form of toxic pollutant, frequently appears in industrial wastewater [1, 2], which normally exists as hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) in water environments [3]. Cr(VI) is also a carcinogenic matter, and considered to be 100 times more toxic than Cr(III) [4-6]. Thus, it is urgent and important to explore an effective technology to remove Cr(VI) from wastewater.

Electrocoagulation (EC), as a promising method for Cr(VI) containing wastewater treatment, has the advantages in no addition of chemicals, small production of sludge and negligible control of process [7-9]. Until now, many types of research have studied the Cr(VI) removal behaviours during EC process [5, 10-12]. Despite empirical operation parameters were done, here still some problems existed. For example, a passive film, consisted of iron and chromium oxides, may form on iron electrodes surface during EC process. This film, in general, increases the energy consumption and therefore leads to a poor removal efficiency of Cr(VI) [13]. Fortunately, it is reported that chloride ions (Cl)’ existing in the treated wastewaters could destroy the passive film [11, 14-16]. However, EC process investigated in these works do not quantitative determined the required amount of Cl for the destruction of the passive film, let alone the optimization of Cl addition to remove Cr(VI).

During EC process, many factors affect the Cr(VI) removal, such as electrodes materials, initial pH, current density, electrolyte concentration, treatment time and temperature [7]. Therefore, the optimization of Cr(VI) removal must consider many operation parameters, which is time consuming
and complex by conventional multifactor experiments. In this circumstance, response surface methodology (RSM) may be a good alternative, as it can provide statistical models that help in understanding the interactions among the parameters [17-19].

The main purpose of this study was to investigate the pitting corrosion of Cl- in EC for Cr(VI) removal. Firstly, the effect of Cl- on Cr(VI) removal was tested by varying Cl- concentration. Then the relationship of Cr(VI) removal and the factors of initial pH, current density and Cl- was assessed. Finally, the optimal operation conditions were determined by RSM.

2. Material and methods

2.1. EC test setup

The EC unit was 2.5 L, as described previously [7], consisting of two iron plates electrodes (structural carbon steel, Q195), each with a dimension of 200 mm ×50 mm ×1 mm and an effective area of 75 cm². The distances of the electrodes were fixed at 20 mm. A direct-current power (RIGOL DP1116A) was used to supply a defined constant current. The simulated Cr(VI) containing wastewater was prepared by dissolving the required amount of K₂Cr₂O₇ (Merck, Germany) in deionized water, and the conductivity of the wastewater was adjusted by adding NaNO₃ solutions. The pH of solution was adjusted by the addition of NaOH or HNO₃ solutions and measured by a pH meter (Mettler FE20K, Switzerland). A stirring rate of about 200 rpm was set to ensure the homogeneous mass transfer. The reaction was set at 40 min, regulated by a microcomputer timer switch (TOONE ZYT16, China). By the end of each run, the sample taken from the reactor was used to determine the amount of chromium and dissolved iron, following the steps in the literatures [7, 13, 20]. The structural characteristics of the surface of iron electrode after electrolysis was evaluated by ESEM (Quanta 200 FEG, FEI, US). All experiments were performed at 20±1 °C.

2.2. Chloride ions addition experiments

The influence of Cl- on Cr(VI) removal in EC was studied by varying the Cl-concentration (0-150 mg L⁻¹). During the experiments, the produces were the same as the section 2.1 described.

2.3. RSM experiments

The central composite design (CCD) was chosen to optimize the factors of initial pH (x₁), applied currents (x₂) and Cl- concentration (x₃) on Cr(VI) removal efficiency (y₁) in EC process. All factors were controlled at five levels. The Cr(VI) removal efficiency was set as response variable, and fitted by a second-order model in the form of quadratic polynomial equation, as reference in literatures [7, 13, 16]. The Design-expert 7.1.3 (Stat-Ease Inc., USA) was used to frame the optimized experiments, as shown in Table 1.

| Variables          | Codes | Coded levels |
|--------------------|-------|--------------|
| Initial pH         | x₁    | 1.00 2.62 5.00 7.38 9.00 |
| Applied currents (A)| x₂    | 0.400 0.640 1.000 1.360 1.600 |
| Chloride ions (mg L⁻¹) | x₃    | 0.00 20.27 50.00 79.73 100.00 |

3. Results and discussions

3.1. Cr(VI) removal in different concentration of chlorine ions

Figure 1 presented the change of Cr (VI) removal efficiency within different concentration of Cl-. As shown, poor Cr(VI) removal capacity was observed without the addition of Cl-. These might be due to a passive film formed on the anode surface, which prevented iron dissolution and electron transfer, as evidenced in other studies [11, 15, 21]. However, Cl- addition increased Cr(VI) removal (Figure 1).
The Cr(VI) removal efficiency first increased with the increase of Cl\(^-\) concentration, then reached a maximum (~100\%) at 50 mg L\(^{-1}\) Cl\(^-\), and finally remained constant when further increased the concentration of Cl\(^-\) (50-150 mg L\(^{-1}\)).

The change of the amount of dissolved iron during EC process is also observed in Figure 1, displacing a similar trend as Cr(VI) removal efficiency. Note that the amount of dissolved iron approximated the theoretical one (696.48 mg), which was calculated based on Faraday’s law [7], when the addition of Cl\(^-\) was above 50 mg L\(^{-1}\). Therefore, it is assumed that Cl\(^-\) addition might act as an enhancement agent for Cr(VI) removal owing to increasing the dissolved irons.

![Figure 1](image1.png)

**Figure 1.** The Cr(VI) removal efficiency and dissolved iron within Cl\(^-\); initial pH 5, applied currents 1A, application time 40min, stirring speed 200 rpm and 20\(^\circ\)C.

The ESEM was used to evaluate the structural characteristics of the surface of iron electrode after electrolysis within different Cl\(^-\) containing solutions (Figure 2). As showed, in the absence of Cl\(^-\) (Figure 2a), only a small range of bright parts were detected, at which iron dissolved. Most of the other parts looked dull, suggesting passive film was formed, which prevented iron dissolution. In contrary, other anode surfaces exhibited pitting corrosion (Figure 3b-d). The size and distribution of the pitting depended on the concentration of Cl\(^-\). Specifically, as Cl\(^-\) concentration increased from 20 to 150 mg L\(^{-1}\), pitting turned to be bigger and deeper, along with higher distribution density. ESEM analysis further demonstrated that Cl\(^-\) could destroy the passive film and initiate pitting corrosion.
Figure 2. Environmental scanning electron microscope graphs of iron anodes after electrolysis of 40 min in different Cl⁻ containing solutions. Electrolyte: (a) NO₃⁻ 1000 mg L⁻¹ without Cl⁻, (b) 20 mg L⁻¹ Cl⁻, (c) 50 mg L⁻¹ Cl⁻, (d) 150 mg L⁻¹ Cl⁻, initial pH 5.0, 1.000 A, 200 rpm and 20°C.

3.2. Analysis of RSM design
The results of CCD design of initial pH (x₁), applied currents (x₂) and Cl⁻ concentration (x₃) and the corresponding response value (Cr(VI) removal efficiency (y₁)) are presented in Table 2.

Table 2. CCD design and response value.

| Run | Code values | Real values | Response |
|-----|-------------|-------------|----------|
|     | x₁ | x₂ | x₃ | x₁ | x₂ (A) | x₃ (mg L⁻¹) | y₁ (%) |
|-----|-----|-----|-----|-----|-------|--------------|--------|
| 1   | -1.00 | 1.00 | 1.00 | 2.62 | 1.357 | 79.73 | 99.99 |
| 2   | 0.00  | -1.68 | 0.00 | 5.00 | 0.400 | 50.00 | 61.77 |
| 3   | -1.00 | 1.00 | -1.00 | 2.62 | 1.357 | 20.27 | 63.99 |
| 4   | 0.00  | 0.00 | 0.00 | 5.00 | 1.000 | 50.00 | 99.99 |
| 5   | -1.00 | -1.00 | 1.00 | 2.62 | 0.643 | 79.73 | 89.95 |
| 6   | 1.00  | 1.00 | 1.00 | 7.38 | 1.357 | 79.73 | 73.69 |
| 7   | 0.00  | 0.00 | 0.00 | 5.00 | 1.000 | 50.00 | 99.99 |
| 8   | 0.00  | 0.00 | 0.00 | 5.00 | 1.000 | 50.00 | 99.99 |
| 9   | 1.00  | -1.00 | 1.00 | 7.38 | 0.643 | 79.73 | 73.69 |
| 10  | -1.00 | -1.00 | -1.00 | 2.62 | 0.643 | 20.27 | 73.69 |
| 11  | -1.68 | 0.00 | 0.00 | 1.00 | 1.000 | 50.00 | 99.99 |
| 12  | 1.00  | 1.00 | -1.00 | 7.38 | 1.357 | 20.27 | 31.56 |
| 13  | 0.00  | 0.00 | 0.00 | 5.00 | 1.000 | 50.00 | 99.99 |
| 14  | 0.00  | 0.00 | 1.68 | 5.00 | 1.000 | 100.00 | 99.99 |
| 15  | 0.00  | 0.00 | 0.00 | 5.00 | 1.000 | 50.00 | 99.99 |
| 16  | 0.00  | 0.00 | -1.68 | 5.00 | 1.000 | 0.00 | 28.21 |
| 17  | 1.00  | -1.00 | -1.00 | 7.38 | 0.643 | 20.27 | 41.54 |
| 18  | 0.00  | 0.00 | 0.00 | 5.00 | 1.000 | 50.00 | 99.99 |
| 19  | 0.00  | 1.68 | 0.00 | 5.00 | 1.600 | 50.00 | 99.99 |
| 20  | 1.68  | 0.00 | 0.00 | 9.00 | 1.000 | 50.00 | 97.71 |

The ANOVA of this model was analyzed by using Fisher’s statistical method. The results showed that the F-value (11.37) was greater than F₀.₀₁(20, 29)=2.57, p<0.01, thus indicating the model was highly significant. Then, an equation (equation 1) was obtain based on the above results, which can be used to explain the relationship of response value (y₁) and the other 3 factors (x₁-x₃). The corresponding significant coefficient were shown in Table 3.

\[ y_1 = 100.20 - 7.38x_1 + 4.74x_2 + 18.85x_3 + 4.01x_1x_2 + 8.05x_1x_3 + 9.01x_2x_3 - 1.74x_1^2 - 8.09x_2^2 - 14.02x_3^2 \]  

(1)

Table 3. Significance coefficient of the model for corresponding variables.

| Variables | Regression coefficients | Degrees of freedom | Standard error | p     |
|-----------|------------------------|-------------------|---------------|-------|
| x₁        | -7.38                  | 1                 | 2.76          | 0.0235|
| x₂        | 18.85                  | 1                 | 2.77          | <0.0001|
| x₃        | 8.05                   | 1                 | 3.61          | 0.0498|
| x₁x₂      | 9.01                   | 1                 | 3.61          | 0.0316|
| x₁x₃      | -8.09                  | 1                 | 2.69          | 0.0132|
| x₂²       | -14.02                 | 1                 | 2.69          | 0.0004|
Among the first-order terms, initial pH and Cl\textsuperscript- concentration were significant. As discussed previously (section 3.1), Cl\textsuperscript- addition could improve Cr(VI) removal. For initial pH, similar result was also gained in previous studies, in which acidic pH resulted in a high Cr(VI) removal capacity in EC process [15]. In the higher-order terms, applied current and Cl\textsuperscript- concentration were significant. Current was an important factor in EC process, and it has been suggested that higher Cr(VI) removal was observed when low currents was applied compared to high currents [3]. As to interaction terms, the initial pH and Cl\textsuperscript- concentration, applied currents and Cl\textsuperscript- concentration were significant. Figure 3(a) revealed Cr(VI) removal efficiency with varying Cl\textsuperscript- concentration and applied currents. It can be seen that Cr(VI) removal efficiency increased significantly with the increase of Cl\textsuperscript- concentration at high currents, however, it was not significant at the low currents. The passive film formed at high currents [13] was likely the reason, for Cr(VI) removal efficiency could be remarkably improved by means of increasing Cl\textsuperscript- concentration. However, the passivation was negligible at low applied currents, so the effect was not significant. Figure 3(b) revealed Cr(VI) removal efficiency with varying Cl\textsuperscript- concentration and initial pH. As observed, the Cr(VI) removal efficiency increased with the decrease of initial pH at low Cl\textsuperscript- concentration, likely due to the chemical dissolution of iron in acidic condition promoted the Cr(VI) removal [7].

![Figure 3](image)

**Figure 3.** The graph of Cr(VI) removal efficiency and (a) chloride concentration-applied currents, (b) chloride concentration-initial pH.

### 3.3. Optimization of EC process.

In this section, the main purpose was to verify the optimization results obtained by RSM. Firstly, the target value of Cr(VI) removal efficiency was set at 100 %, then the optimal condition was gained by calculating through the regression equations (equation (1)): initial pH at 5.24, applied currents at 0.914 A and Cl\textsuperscript- concentration at 54.37 mg L\textsuperscript-. According to the data of verification test, the Cr(VI) removal efficiency was 99.98 % under the above optimal condition. Thus, it is reasonable to conclude that the RSM was useful in optimizing Cr(VI) removal in EC process.

### 4. Conclusions

The experimental results shown that Cl\textsuperscript- addition promoted the Cr(VI) removal, owing to the increase of dissolved iron by pitting corrosion, as demonstrated through ESEM analysis. According to RSM, the optimal operation conditions were initial pH at 5.24, applied currents at 0.914 A and Cl\textsuperscript- concentration at 54.37 mg L\textsuperscript-, which could achieve Cr(VI) removal efficiency of 99.98 %.

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