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Study on Treatment of High Chromium Industrial Wastewater by Pulsed Field-Coprecipitation Method

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***Abstract*—Chromium pollution poses a serious threat to the safety of human beings and animals. The traditional method of treating Chromium-containing wastewater is difficult to achieve the purpose of removing chromium depth, In this paper, the removal of chromium in high-chromium industrial wastewater was studied by pulsed electric field-coprecipitation method, and the removal efficiency of chromium was explored in action time , pulse voltage and duty cycle. The experimental results show that the action time is 4min, the pulse voltage is 75V, the duty ratio is 10%, and the content of chromium is reduced from 34.9mg/L to 0.0028mg/L Chromium removal rate of up to 99.92%.**

Keywords- pulsed electric field; coprecipitation; chromium; high chromium wastewater

I. INTRODUCTION

Chromium-containing wastewater generated in the electroplating industry is one of the most serious hazards [1], the main forms of chromium in water are Cr^{6+} and Cr^{3+}, in which the toxicity of Cr^{6+} is 100 times that of Cr^{3+} [2]. Cr^{6+} directly affect the body's oxidation, hydrolysis and other metabolic processes [3]. When the Cr^{6+} intake of more than 0.1 mg/L will lead to human poisoning [4], long-term exposure to chromium solution, containing lead to dermatitis, eczema, "chromium sores" [5-8]. The traditional methods on the treatment of chromium containing wastewater with Precipitation, adsorption, etc [9-10]. However, these methods are difficult to reduce the total chromium content to 1.5 mg/L [11], the emission concentration higher than the national emission standard 1 mg/L, can't achieve the purpose of deep chromium removal. In order to find out the effective and efficient method of removing chromium, this paper uses pulsed electric field-coprecipitation method to treat the high chromium industrial wastewater, and explores the best chrome removal efficiency in the action time, pulse voltage and duty cycle.

II. EXPERIMENTAL STUDY ON THE TREATMENT OF HIGH CHROMIUM INDUSTRIAL WASTEWATER BY PULSED ELECTRIC FIELD-COPRECIPITATION METHODE

Pulsed electric field-coprecipitation method is the application of pulsed electric field in the high chromium industrial wastewater, so that Cr^{6+} anion clusters in the positive plate aggregation, under the action of reducing agent Cr^{6+} is restored. Formation of insoluble $Cr(OH)_3$ precipitates from water. At the same time, The $Fe(OH)_3$ floc formed adsorbent during the reduction. Coprecipitation is an integrated precipitation process. During the process of polymer precipitation, chromium can be precipitated with the hydrolyzate by adsorption, encapsulation and complexation. The chemical precipitation and physical adsorption precipitation interaction method known as the pulse electric field - coprecipitation method.

The time of action is an important electric field parameter of pulsed electric field-coprecipitation method. The effect of different working time on the removal rate of chromium in industrial wastewater has a direct impact.

A. The Effect of Different Action Time on the Efficiency of Chromium Removal

Water samples taken from a electroplating factory production wastewater, pH at about 6, the initial total chromium concentration of 34.9 mg/L. Selection of Cu, C material as a positive and negative plates.

Take 1 L of water sample, adjust the pH to 3-4, and into the reaction tank. adjust the pulse voltage of 100V, pulse width of 3ms, period of 30ms, the plate spacing of 20cm. The action time was set to 2 min, 4 min, 6 min, 8 min, 10 min, 30 min and 60 min, respectively, After 30 seconds of electrification, and the samples were detected by the addition of $FeSO_4 \cdot 7H_2O$ solution at the ratio of $m_{FeSO_4 \cdot 7H_2O} : m_{Cr^{6+}} = 1:1$. Sampling inspection. See Table I, Figure 1.

TABLE I. EFFECT OF ACTION TIME ON REMOVAL EFFICIENCY OF CHROMIUM REMOVAL

Action time(min)	2	4	6	8	10	30	60
Initial chromium content(mg/L)	34.9	34.9	34.9	34.9	34.9	34.9	34.9
Chromium content after treatment (mg/L)	1.759	0.386	0.272	0.186	0.180	0.174	0.176
Chromium removal rate (%)	94.96	98.89	99.22	99.47	99.48	99.50	99.49

TABLE II. EFFECT OF PULSE VOLTAGE ON THE EFFICIENCY OF REMOVING CHROMIUM REMOVAL

Pulse Voltage (V)	50	75	100	125	150
Initial chromium content (mg/L)	34.9	34.9	34.9	34.9	34.9
Chromium content after treatment (mg/L)	0.296	0.028	0.386	0.140	0.296
Chromium removal rate (%)	99.15	99.92	98.89	99.60	99.15

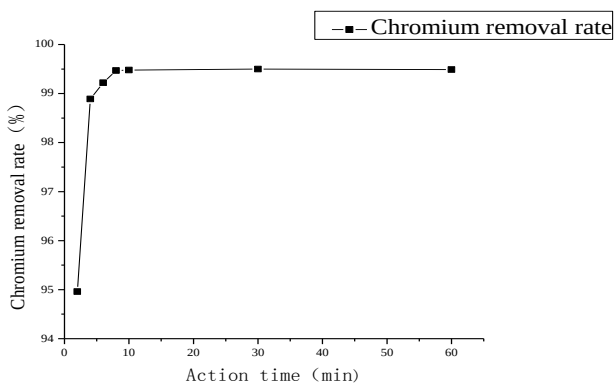

Figure 1. Chromium removal rate along with the change of action time.

From Table I, Figure 1 can be seen that the removal rate of chromium in wastewater with the increase with the time of action, After the action time reaches 4min, the rise tends to be flat, chromium removal rate gradually becoming stable. The removal rate of chromium in wastewater was 98.89% at 4 min, the content of chromium in waste water was reduced from 34.9 mg/L to 0.386 mg/L, and the chromium content was below the national emission standard. Although the removal rate of chromium is still increasing with the lengthening of time, the longer the action time is, the more energy is consumed, and the higher the time cost, the higher the production cost. Therefore, the best time for chromium removal should be 4min.

B. The Influence of Different Pulse Voltage on Chromium Removal Efficiency

Taking into account the pulse generator in the FET can withstand the current is limited, and the voltage is too high to conducive energy saving, the experimental pulse voltage is generally below 150V.

Take 1 L of water sample, adjust the pH to 3-4, adjust the pulse width of 3ms, period of 30ms, the plate spacing of 20cm and action time 4min.The pulse voltage was 50V, 75V, 100V, 125V, 150V . After 30 seconds of electrification, $FeSO_4 \cdot 7H_2O$ solution was added near the positive plate, the ratio was $m_{FeSO_4 \cdot 7H_2O} : m_{Cr^{6+}} = 1:1$ .the end of the experiment, sampling detection. See Table II, Figure 2.

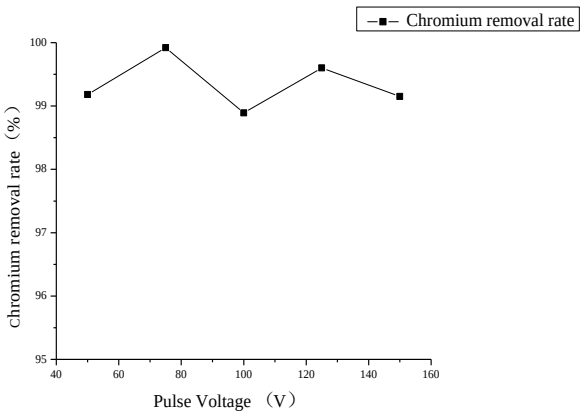

Figure 2. Chromium removal rate along with the change of Pulse Voltage.

From Table II, Figure 2 can be drawn: the choice of different pulse voltage, the water content of chromium in the national emission standards 1mg/L below. Although the concentration of chromium after treatment fluctuates below 0.386 mg/L, the treatment effect can be achieved. In the follow-up study, this experiment can be repeated for better analyzing towards the cause of the fluctuation. In the further experiments, 75V was chosen as the optimum voltage parameter.

C. *The Influence of Different Duty Ratio on Chromium Removal Efficiency*

Duty cycle is the ratio of the pulse width to the period of the pulsed electric field. In order to select the ideal reaction condition, the duty cycle is chosen as the experimental factor. The action time is 4min, the pulse voltage is 75V.

Take 1 L of water sample, and the pH value was adjusted to 3-4, and period of 30ms. The distance between the plates was 20cm and the duty cycle was 10%, 20%, 30%, 40% and 50% respectively. After 30 seconds of electrification, $FeSO_4$ $7H_2O$ solution was added near the positive plate, the ratio was

$m_{FeSO_4 \cdot 7H_2O} : m_{Cr^{6+}} = 1:1$ .After the end of the experiment, samples were taken for testing. See Table III, Figure 3.

TABLE III. EFFECT OF DUTY RATIO ON THE EFFICIENCY OF REMOVING CHROMIUM REMOVAL

Duty Ratio	10%	20%	30%	40%	50%
Initial chromium content (mg/L)	34.9	34.9	34.9	34.9	34.9
Chromium content after treatment (mg/L)	0.028	0.216	0.328	0.360	0.350
Chromium removal rate (%)	99.92	99.38	99.06	98.97	99.00

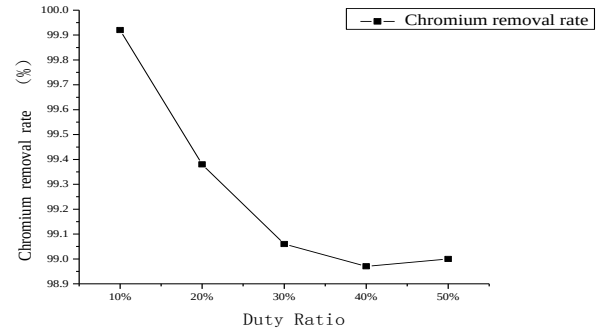

Figure 3. Chromium removal rate along with the change of Duty Ratio.

As can be seen from Table III, Figure 3, the chromium content in wastewater after treatment and duty cycle is closely related. In the same period, the smaller the duty cycle, pulse width is narrower, the role of an electric field within a shorter period of time, the higher the removal rate of chromium. This is because the smaller the duty cycle is, the smaller the solution concentration difference polarization is conducive to the diffusion, promote the removal of chromium, but also reduces energy consumption. the best duty cycle for chromium removal should be 10% .this time the removal rate of chromium 99.92%.

III. SUMMARY

In this paper, the pulsed electric field-coprecipitation method was used to study the removal of chromium from high chromium industrial wastewater, and the removal efficiency of chromium was discussed. The action time, pulse voltage and duty cycle on the removal of chromium were studied. Concluded as follow:

1.Pulsed electric field-coprecipitation method is a kind of efficient chromium removal method. When the action time is 4min, the pulse voltage is 75V and the duty ratio is 10%, the content of Cr in the wastewater decreases from 34.9mg/L to 0.028mg/L. Chromium removal rate of up to 99.92%, to the national emission standards.

2. Treatment of high chromium industrial waste water by pulsed electric field-coprecipitation method. The chromium content in treated wastewater decreased with the increase of working time, and the removal rate of chromium was increased.

3. Pulsed electric field-coprecipitation method has not yet been reported in domestic and foreign literatures, which provides new ideas and new methods for the treatment of industrial high chromium wastewater.

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