Experimental study on the treatment of chromium containing wastewater by electric flocculation

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Abstract. For the ecological environment of serious pollution of wastewater containing chromium, made of aluminum plate electrocoagulation as chromium-containing wastewater treatment equipment, the effect of current density, treatment time, electrode spacing and other factors on the treatment effect. Experimental results show that the electro-flocculation process, a current density of 1.5, the initial pH of 6.0 and an electrolysis time of 1 hour, the plate spacing of 1cm optimal removal efficiency can reach 64%. In the electrocoagulation process, with increasing current density, electrolysis time, the metal ion removal increased; reduced electrode spacing, making the removal of heavy metal ions to achieve better results.

Keywords. Chromate waste water, Electric flocculation, Influence factor, Removal rate

1. Introduction
Chromium ions are highly toxic and can invade human bodies through many channels and accumulate in the human body. Chromium compounds have a carcinogenic effect. The chromium in the water can accumulate in the bones of the fish, and Cr$^{3+}$ is more toxic than Cr$^{6+}$. The concentration of 3 mg/ L was fatal to freshwater fish, and the concentration of 0.01mg / L could cause some aquatic organisms to kill and inhibit the self-purification of water body. If chromium is used to irrigate farmland, chromium will accumulate in plants, and the digestibility of organic matter in the soil is inhibited, resulting in agricultural production. The pollution of chromium is mainly caused by industry. Therefore, all countries for wastewater, emissions of fishery water quality, irrigation water, surface water and drinking water of the chromium content, has the strict stipulation. However, for the treatment of chromium, there are many problems such as chemical [1], biological [2], adsorption [3], ion exchange [4] and photo catalysis [5], such as low efficiency, large dosage, large amount of waste residue and complicated operation.

Wastewater by electric flocculation treatment, which is characterized by using soluble anode such as aluminum or iron as a sacrificial electrode by chemical reaction produces both flotation needed and bubbles in the solution hydrolysis and polymerization to generate a series of polynuclear hydroxyl
complex and hydroxide as flocculants and flocculation. Electric flocculation generally does not need to add chemicals, because the equipment needed is small, the floor area is not wide, the operation is simple and flexible, and the amount of sludge is small. Subsequent processing is not very complicated. In recent years, electrocoagulation has been applied to treat electroplating wastewater, chemical wastewater, printing and dyeing wastewater, pharmaceutical wastewater, tannery wastewater, papermaking wastewater and other industrial wastewater and water purification at home and abroad. Besides, electric flocculation can remove part of COD and improve the biodegradability of wastewater. It can also be used in a pretreatment before biochemical method. Therefore, in the process of wastewater treatment, the electrocoagulation reaction is a very important part.

2. Experimental section

2.1. A subsection

2.1.1. Reagent. potassium dichromate (CR); sodium hydroxide (CR); sodium chloride (CR); nitric acid, hydrochloric acid (AR); ammonium chloride (AR); two - two carbon acyl hydrazine (AR); Potassium Permanganate (AR); acetone; sulfuric acid.

2.1.2. Instrument. UV spectrophotometer and color tube plug 50ml specifications; pipette of cylinder; 250ml; 250mL conical flask; volumetric flask etc.

2.1.3. Experimental research equipment. Reaction groove and plate self-design.

2.1.4. Test water distribution. The artificial wastewater is used. Potassium dichromate (K2Cr2O7, 0.2829g, GR) for water dissolved into 1000ml volumetric flask, dilute with water to shake line. Each milliliter of solution contains 0.100mg six valence chromium.

2.2. Experimental principle

2.2.1. Electric flocculation. Under the action of external voltage, aluminum is used as the electrode plate. The captions produced in the solution are hydrolyzed and polymerized to produce a series of polynuclear hydroxyl complexes and hydroxides, which react with six valet chromium ions to form flocculent precipitates and remove six valence chromium ions.

Anodic reaction: \[ \text{Al} - 3\text{e}^- \rightarrow \text{Al}^{3+} \]

Catholic reaction: \[ \text{Al}^{3+} + n\text{H}_2\text{O} \rightarrow \text{Al(OH)}_n^{3-n} + n\text{H}^+ \]

The prepared experimental wastewater in a 1000ml beaker, connect the power supply into the electrode plate, then add Nalco to increase the rate of the first to do the conductive effect of current intensity on chromium removal experiment, firstly the current to 0.5A, electrolysis for 30 minutes, the interval is 20mm and the initial pH at this time should be 6. The electrolysis solution was placed in a static solution, then the simulated waste liquid was prepared. The current was adjusted to 1, 1.5, 2, 2.5A electrolysis and static, and then the supernatant was used to do the absorbance test. The comparison between current intensity and current intensity is shown in Table 2.1. When electrolysis time is applied to the removal rate, the electrolysis time should be 10, 20, 30, 40, 50 and 60min when the current intensity is 1.5A, the interelectrode spacing is 20mm, and the initial pH is 6. The electrolytic solution after static, then the supernatant spacing influence on the removal rate of the experiment, the electric strength and stability to 1.5A, the initial pH was 6, the electrolysis time is 30min under the condition of the electrode plate distance respectively to 1, 2, 3. 4, 5cm under the condition of electrolysis, static, and then do the absorbance of supernatant test; finally, initial PH on chromium removal effect, the current intensity is 1.5A, electrolysis time of 30min, the
plate spacing is 2cm, respectively, the initial pH of wastewater 4.0, 5.0, 6.0, 7.0, 8.0 electrolysis. After the electrolysis of the solution static, and then take the supernatant to do the absorbance test.

Table 1. Comparison table of current intensity and current density per unit area in the test

| Current intensity(A) | 0.5  | 1    | 1.5  | 2    | 2.5  |
|----------------------|------|------|------|------|------|
| Current density per unit area(mA/cm²) | 16.67 | 33.33 | 50   | 66.67 | 83.33 |

2.2.2. Measurement of absorbance. The supernatant of the wastewater after the treatment was filtered out, and the absorbance was measured by a spectrophotometer. Finally, the chromium content was calculated.

2.2.3. Experimental device. The electric flocculation reaction in a capacity of 1000 mL ordinary beaker, cathode and anode for a piece of aluminum electrode, two parallel plates vertically into the beaker, the purity of aluminum is 99%, Noah to adjust the sample pH value, after the opening of the power supply wiring, through a magnetic stirrer to prevent polarization the electrolyte produced by adjusting the voltage and current value. The quality of chromium was measured by ultraviolet spectrophotometer at a certain time of sampling at a certain time.

3. Results and discussion

3.1. Effect of current intensity on chromium removal rate

The effects of current intensity on 0.5, 1, 1.5, 2, 2.5A, 30min time, initial pH 6, electrode spacing 2cm, and six valence chromium concentration were 100mg/L, respectively. The effect of current intensity on the removal of six valent chromium is shown in Fig. 1.

![Figure 1. Effect of current intensity on Removal rate of six valent chromium](image-url)
Figure 1 shows that the changes to the 1.5A 0.5A in the current intensity, with the increase of current intensity, chromium removal efficiency increased gradually, when the current reaches 1.5A, the removal efficiency reached the maximum 57.4%; continue to increase the current intensity changes from 1.5A to 2.5A, the chromium removal efficiency of anti-decreased. The possible reason is that current is the power source of electric flocculation process of dissolution, flocculation and flotation plate, determines the amount of flocculants produced, but also determines the bubble rate, so the current intensity began to increase a flocculants producing volume increased, the bubble rate increased, the flocculation capacity strengthened, thereby quickly and effectively the removal of heavy metal ions. When the current intensity continued to increase more than 1.5A removal rate decreased, probably because the current strength is too large to accelerate the polarization and passivation of the electrode, causing unnecessary side reactions: anodic aluminum to produce too much Al3+, Al and OH- in the solution (OH) 3 flock, loose structure is not easy to precipitate, influence the flocculation effect of flocculants production decreased significantly; in addition the cathode hydrogen produced more and more bubbles, flotation effect on flock collision acceleration increases, while larger bubbles are prone to rupture with shear effect on flock flocculation effect, lead to decline.

The current intensity of the anode directly affects the reaction rate of anodic oxidation. Under the same conditions, the electrochemical reaction speed is faster with the increase of anode current intensity, but the increase of current intensity will accelerate the passivation of electrode.

3.2. The effect of treatment time on the removal rate of chromium

The electrocoagulation equipment plate spacing is 2cm, the current intensity is 1.5 A, the initial pH value is 6, six chromium concentration is 100mg/L, the water flow control that the treatment time were 10, 20, 30, 40, 50, 60min, different treatment time of total chromium and chromium removal rate of six the effect is shown in figure 2:

Figure 2 shows that the current control situation under the certain strength (1.5A), time increased from 10 min to 30min, the treatment efficiency of equipment six chromium obviously and with time increasing, when the processing time was 30 min, the treatment effect of equipment to achieve the best condition (removal rate 63.4%). After 30min, the further prolongation of the treatment time was not obvious to the removal rate. This is mainly the effect of electrocoagulation reached saturation point, so the reaction time increases, the effect is not unlimited growth; in addition, with the increase of time, the metal plates are prone to form a passivation layer of loose protective film, influencing the quantity of dissolved aluminum electrode and free radicals, resulting in aluminum ions and reduce the amount of flocculants the effect of oxidation decreased, continue to increase the reaction time on the removal effect of little significance. And with the increase of energy consumption, the cost of processing increases as the time increases. Therefore, the time control of electrolysis is suitable for 30min.

Longer reaction time can bring a stable treatment effect, but the volume of the device will increase. Of course, the reaction time is too short, and the treatment effect is difficult to guarantee. The
relationship between processing time and current intensity is very close. The higher the current intensity is, the faster the treatment rate is, the shorter the time needed to process, but it will bring about the increase of the side reaction process and the increase of energy consumption. Therefore, the optimization of the combination of processing time and current intensity is crucial to the engineering application of the equipment.

3.3. Influence of electrode plate spacing on chromium removal rate
The electrode spacing has the most direct influence on the current, the electrode spacing is small, the electric flocculation treatment effect is good, but the energy consumption is large, and the small spacing is not conducive to the processing of the equipment. The electrode spacing increases and the resistance increases, though the energy consumption is small, but the electric flocculation effect is also poor. Nevertheless, the spacing between electrode plates should not be too small when doing experiments, because the space between electrode plates is too small to increase the possibility of clogging of scum, which is easy to cause short circuit damage between the electrodes and cause damage to the equipment. Therefore, the electrode spacing is 1, 2, 3, 4 and 5 cm, respectively, at pH value of 6, current intensity of 1.5 A, and electrocoagulation time of 30 min. The experimental results under action conditions are shown in Figure 3.

Removal rate%  

![Figure 3. Effect of electrode plate spacing on the removal rate of six valet chromium](image1)

![Figure 4. The effect of initial pH on the removal rate of chromium](image2)

We can see from Figure 3, the plate spacing is 1cm to 2cm growth, increasing the distance between the chromium removal rate increases, the plate spacing is 2cm and has a maximum value of 61.5%, with the plate spacing in 2 to 5cm increases, the chromium removal rate decreases with the increasing distance between the plates from the reason may be too small in exchange, solution between the plates
to reduce the amount of flocks in between the plates stacked easily blocked, which not only reduces the effective contact area is not conducive to the flocculation, flocculation and sedimentation, resulting in poor removal effect, but also easy to cause short circuit plate. As the distance between plates increases, the ion migration distance increases gradually, and the migration resistance increases. It is easy to cause concentration difference polarization. The current is used to overcome resistance, resulting in low utilization rate and low treatment effect. The larger the distance between the plates, the higher the voltage and the increase of the energy consumption.

The electrode spacing is small, the interelectrode resistance decreases, the strength of the current increases, which leads to increased number of flocculants and hydroxyl ions at the same time, becomes smaller in the plate spacing, gas produced cathode electrolysis bubbles to chromium aluminum complexes formed at the anode electrode reaction leads to the rapid rise in speed, accelerate the further dissolution of aluminum anode so, the metal ion has good removal effect. In the actual operation process of electrode spacing cannot be too small, too small to make the electrode spacing between the plates in the scum jam, cause a short circuit and damage the equipment electrode spacing is too large, the electrolysis time is too long, will be due to alumina complex formation in the anode region covering the anode surface and easy to block the formation of passivation, electrochemical reaction. When the distance is 2cm, the removal rate is high and the distance is too short to destroy the equipment. In comprehensive consideration, it is suitable for the electrode spacing to be 2cm.

3.4. The effect of initial pH value on the chromium removal rate

The electrode spacing is 2cm, the current intensity is 1.5A, and the power on time is 30min. The initial pH of simulated wastewater is adjusted to 4.0, 5.0, 6, 7 and 8, respectively, and the removal rate of chromium is compared. The test results are shown in Figure 4:

From Fig. 4, we can see that when the current intensity is 1.5A, the electrolysis time is 30min and the spacing between plates is 2cm, the removal rate of the six valence chromium increases with the increase of ph. When pH reaches 6, if the pH continues to increase, the treatment effect will decrease. When the pH value is 4–6, the removal rate of chromium can reach more than 60%, and it tends to be stable. When pH is 6, the removal rate of the six valent chromium is the highest. When the pH value is 7–8, the removal rate of chromium decreases slowly with the increase of ph. The study shows that the treatment of six valent chromium by electrocoagulation is the first reduction of six valence chromium into trivalent chromium. When the anode plate is aluminum, under the action of electric field, aluminum ions are anodic dissolved to produce aluminum hydroxide and its multinuclear colloid through hydrolysis reaction, so as to capture trivalent chromium and its hydroxide. The pH value has a great influence on the formation of multi-core colloids, so the effect of pH on the treatment effect is larger, especially in the process of electrocoagulation. Besides, trivalent chromium is amphoteric. It can dissolve both acid and alkali. The high pH value will make the precipitated chrome re dissolved and reduce the removal rate. Therefore, pH should be controlled between 6~7.

4. Conclusion

This study compares the direct effects on the rate of current intensity, electrolysis time, electrode spacing and size of initial pH on chromium removal, through this experiment, three factors combined with the actual operation, energy consumption and metal removal rate, the optimal technological conditions of flocculation in treatment of chromium containing waste water is: the initial pH= 6, the current density is 50 mA/cm2, the electrode distance was 2 cm, the processing time for 30min.

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