Study on the Treatment of Aluminum Milling Wastewater by Electrode-Fenton Method

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Abstract: Aluminum alloy chemical milling wastewater is the wastewater produced in the washing process after aviation aluminum chemical milling. According to its characteristics of high alkalinity, high concentration of organic compounds and difficult biochemical treatment, the electro-Fenton method was used in this study. Electro-Fenton method mainly is the Fenton reaction between Fe²⁺ and hydrogen peroxide produced by electrolytic dissolved oxygen to produce HO·, which reacts with organic pollutants and mineralizes. In the experiments, activated carbon fiber and Ti/RuO₂−IrO₂ were used as the cathode and the anode, respectively. The experiments showed that the optimal initial pH value of degradation was 3, voltage was 40V, and the concentration of Fe²⁺ was 0.5mmol/L, plate spacing was 5cm, the concentration of Na₂SO₄ was 10g/L, the aeration intensity was 125L/h, and the reaction time was 120min, the average removal rate of COD was over 50%. Under optimum conditions, the study established a dynamic model and deduced that it could be described with first order dynamic model. The fitting equation is: $C_t = C_0 \exp(-1.2879C_0-0.8253t)$.

1. Introduction
Aluminum alloy chemical milling process is a key technology widely used in the surface treatment of aluminum alloy in aerospace industry [1-2]. The chemical milling wastewater produced in the washing process after aluminum material chemical milling is the high concentration of alkaline organic wastewater. If it discharges directly into the environment, it will destroy the ecological balance and even endanger human health.

Conventional wastewater treatment methods include physical, chemical and biological methods, acid-base neutralization, flocculation, adsorption, chemical precipitation and membrane separation technology [3-4]. Aluminum alloy chemical milling wastewater is high alkalinity and high organic concentration, so it is difficult to treat directly by biological method. Previously, people used the Fenton method to treat high concentration organic wastewater [5-6], which is to add Fe²⁺ and hydrogen peroxide reagent manually. Strong oxidant HO· was produced, which oxidizes organic pollutants and turns them into low toxic or non-toxic small molecular substances [7]. In this way, the cost of hydrogen peroxide is high and its transportation is difficult. However, the electro-Fenton can produce H₂O₂ by electrolysis to further participate in Fenton reaction, which not only reduces the cost of hydrogen peroxide and solves its difficulties of transportation, but also has the advantages of strong oxidation ability, fast reaction speed, non-selectivity and no secondary pollution [8].

In the experiment, the electro-Fenton technology was used to treat aluminum alloy milling wastewater. The Ti/RuO₂−IrO₂ electrode was used as the anode, and the activated carbon fiber was used as the cathode. Then the different parameters of the electro-Fenton reaction were investigated,
and the COD removal rate was the main index to determine the optimal reaction conditions. At the same time, the reaction kinetics principle was explored.

2. Material and Methods

2.1 Chemicals
The milling waste water was produced by an aircraft manufacturing company. The main components are sodium hydroxide, sodium sulfide, triethanolamine, sodium aluminate, etc. Analytical grade ferrous sulfate, sodium sulfate, sulfuric acid, potassium dichromate, etc. were obtained from Sinopharm Chemical Reagent Co, Ltd. The titanium plated rhodium plate and activated carbon fiber were purchased Online.

2.2 Device
The electrolytic cell was made of organic glass and has the size of 150×136×270mm with 5L effective volume. The schematic diagram of the experimental device is shown in Figure 1.

2.3 Experimental method
Dispose 4L aluminum alloy milling wastewater diluted 200 times into the electrolytic cell, and add a certain concentration of Na2SO4. Then adjust the pH value with 10% dilute sulfuric acid, add a certain concentration of Fe2+, fix the plate. Finally, open the air compressor and turn on the DC power supply. Sampling at regular intervals for analysis. Activated carbon fiber has been subjected to microwave activation [9]. Since activated carbon fiber has an adsorption effect, all the experiments in this paper have carried out adsorption saturation treatment of activated carbon fiber to remove the influence of its adsorption effect on the experimental results.

2.4 Instruments and Analytical method
Electrolysis were performed with a DC Power Supply (WYK-302B2). The required aeration was provided by an electromagnetic air compressor (ACO-318) and a rotameter (LZBJ10). Drying with electrothermal thermostatic blow dryer (DHG-9246A). The pH was measured using a pH meter. The concentration of H2O2 was determined using the titanium oxalate potassium colorimetric method [10], and the concentration of COD was determined using a fast digestion spectrophotometric method (HJ/T399-2007).

3. Results and Discuss

3.1 The factors of aluminum alloy milling wastewater by Fenton method

3.1.1 Effect of reaction time on COD removal rate. The initial pH value was 3, the voltage was 40V. The dosage of Fe2+ and Na2SO4 was 0.5mmol/L and 10g/L, respectively. The plate spacing was 5cm, the aeration volume was 125L/h, and 4L milling wastewater was treated. The effect of reaction time on the treatment effect was investigated. It was obtained the COD removal rate with the reaction time changes, as shown in figure 2.
Figure 2. Effect of time on COD removal.

The removal rate of COD increased with the increase of time, but its rate of increase decreased gradually after 120 minutes. In the start of the reaction, HO· and H₂O₂ were rapidly produced in the solution, and the concentration was continuously increased, which accelerated the progress of the electric Fenton reaction. With the increase of reaction time, the concentration of organic pollutants in the solution gradually decreased, and the concentrations of intermediate products and by-products gradually increased, resulting in a gradual decrease in the reaction rate. Taking into account the reduction in energy consumption and cost savings, the reaction time was determined to be 120 minutes.

3.1.2 Effect of the initial pH on COD removal rate. Many experiments showed that pH 2-4 more facilitated to the electric-Fenton reaction [11]. Other experimental conditions remain unchanged, the 4L milling wastewater was treated for 120 min. The effect of reaction time on the treatment effect was investigated, as shown in figure 3. As the pH value increased, the COD removal rate increased at first and then decreased. When the pH value was 3, the COD removal rate reached 51.98%. When the pH was less than 3, the concentration of H⁺ was more, and the hydrogen evolution reaction was strengthened, suppressing the production of H₂O₂ and ·OH [12]. When the pH was higher than 3, Fe²⁺ was easily oxidized to Fe(OH)₃, which reduced the yield of ·OH. In addition, under too high pH conditions, H₂O₂ decomposed into O₂ and H₂O, and COD removal rate also decreased.

Figure 3. Effect of pH on COD removal.

3.1.3 Effect of voltage on COD removal rate. Other experimental conditions remained unchanged, the initial pH value was 3. Explore the effect of voltage on the treatment effect. The experimental results were shown in figure 4. When the voltage was 40V, the removal rate of COD was the highest, and when the voltage was greater than or less than 40V, the COD removal rate was decreased. When the voltage was low, the output of H₂O₂ was less. When the voltage was too high, the secondary reactions such as hydrogen evolution and oxygen evolution gradually occupied a dominant position in the system, and the reactor temperature rised, and excess energy was consumed in side reactions. Therefore, the optimal electrolytic voltage was 40V.
3.1.4 Effect of Fe^{2+} dosage on COD removal rate. Other experimental conditions remained unchanged, the voltage was 40V. The effect of the Fe^{2+} dosage on the treatment effect was explored, as shown in figure 5.

![Figure 5. Effect of Fe^{2+} on COD removal.](image)

The removal rate of COD increased with increasing Fe^{2+} dosage, while the removal rate of COD decreased gradually with Fe^{2+} dosage more than 0.5mmol/L. Fenton reaction occurred after Fe^{2+} was added to the system, so COD removal rate increased. However, when the concentration of Fe^{2+} was too large, excess Fe^{2+} reacted with \cdot OH [13]. So the concentration of OH was reduced, the removal rate of COD was decreased.

3.1.5 Effect of plate spacing on COD removal rate. Other experimental conditions remained unchanged, the dosage of Fe^{2+} was 0.5mmol/L. The effect of the plate spacing was discussed. The experimental results were shown in figure 6. The COD removal rate was highest when the plate spacing was 4cm and 5cm, and the COD removal rate decreased with the plate spacing increased gradually. The plate spacing determined the magnitude of the electric field in the electrolytic cell and the potential difference between the solution phase and the anode [14]. When the distance between plates was small, the OH was reduced in the cathode before oxidize the organic pollutants, and the air passing through the narrow space might break through the plate and damage the electrode material. Therefore, the distance between the plates was selected as 5cm.

![Figure 6. Effect of plate spacing on COD removal.](image)
3.1.6 Effect of Na$_2$SO$_4$ dosage on COD removal rate. Other experimental conditions remained unchanged, the plate spacing was 5cm. The effect of Na$_2$SO$_4$ dosage on the treatment effect was investigated, as shown in figure 7.

![Figure 7](image-url)  
**Figure 7. Effect of Na$_2$SO$_4$ on COD removal.**

The COD removal rate increased at first and then decreased with the increase of Na$_2$SO$_4$ dosage with a maximum of 52.35% at 10g/L. With the increase of Na$_2$SO$_4$, the conductivity and current intensity of the solution increased. In this way, the mass transfer and chemical reaction rate in the solution increased, and the removal rate of COD increased. When the concentration of Na$_2$SO$_4$ was further increased, the proportion of side reactions such as hydrogen evolution and oxygen evolution in the system will gradually increase, which makes the removal rate of COD lower.

3.1.7 Effect of aeration rate on COD removal rate. Other experimental conditions remained unchanged, the dosage of Na$_2$SO$_4$ was 10g/L. The effect of aeration rate on the treatment effect was investigated. The experimental results were shown in figure 8.

![Figure 8](image-url)  
**Figure 8. Effect of aeration on COD removal.**

The COD removal rate increased with the increase of aeration rate, reached the maximum with the 125L/h aeration rate, and then the COD removal rate remained basically unchanged. The dissolved oxygen was added to the reaction system through aeration, and the aeration not only sped up the mass transfer process, but also made the reactants more fully accessible. However, when the aeration rate was bigger than 125L/h, its enhancement of the mass transfer process was no longer obvious. Therefore, the aeration in this experiment was 125L/h.

3.2 Dynamic analysis

Some studies [15] have shown that in the electrochemical process, the electrode surface mainly occurs direct oxidation. The change of COD over time can be simplified to the following formula:

$$-dC_o/dt = kC_o^n.$$  
(1)

According to the zero-order, quasi-first, quasi-two, and quasi-three-step reaction kinetic equations, the correlation coefficients corresponding to different reaction orders were calculated, as shown in Table 1.

| Table 1. The calculation of COD degradation kinetics. |
|-----------------------------------------------------|
| time (min) | zero-order | quasi-first | quasi-two | quasi-three-step |
| 0.0 | 25 | 30 | 35 | 40 |
| 62.5 | 37.5 | 42.5 | 47.5 | 52.5 |
| 125.0 | 40.0 | 45.0 | 50.0 | 55.0 |
| 187.5 | 42.5 | 47.5 | 52.5 | 57.5 |
| 250.0 | 45.0 | 50.0 | 55.0 | 60.0 |
The correlation coefficient of the quasi-first reaction was the largest and the linear correlation was good, and the electro-Fenton reaction was judged to conform to the quasi-first reaction kinetics. The kinetic equation was

\[ C_t = C_0 \exp\left(-kt\right) \] (2)

\[ -\ln\left(C_t/C_0\right) = kt \] (3)

Where k was the reaction rate constant. In order to explore the relationship between k and C₀, the wastewater was diluted 100, 150, 200, 250, and 300 times, respectively. The experimental results were shown in Table 2.

Table 2. Experimental results of different COD concentrations.

| inspection indicators | COD concentration (mg/L) |
|-----------------------|--------------------------|
|                       | dilution times           |
|                       | 100                      | 150          | 200          | 250          | 300          |
| raw water             | 1176.39                  | 747.15       | 587.85       | 476.61       | 406.47       |
| effluent              | 727.52                   | 416.48       | 265.33       | 174.71       | 135.72       |
| Ink                   | -5.5203                  | -5.3246      | -5.0162      | -4.7839      | -4.6950      |
| lnC₀                  | 7.0702                   | 6.6163       | 6.3765       | 6.1667       | 6.0075       |

From this, it can be calculated that \( k = 1.2879C_0^{0.8253} \), so the kinetic equation of this reaction was:

\[ C_t = C_0 \exp\left(-1.2879C_0^{0.8253}t\right) \] (4)

4. Conclusion

(1) The optimal reaction conditions were determined by single factor: the pH was 3, the voltage was 40V, the plate spacing was 5 cm, the dosage of \( \text{Fe}^{2+} \) and \( \text{Na}_2\text{SO}_4 \) were 0.5mmol/L and 10 g/L, respectively, the aeration volume was 125 L/h, and the reaction time was 120 min. Under this condition, the average removal rate of COD was over 50%.

(2) The experimental and kinetic calculations showed that the reaction was in accordance with the first-order kinetics model, the correlation coefficient \( R^2 \) was 0.9904, and the linear correlation was good. The kinetic equation as follow:

\[ C_t = C_0 \exp\left(-1.2879C_0^{0.8253}t\right) \]

Through being compared with experimental data, it was proved that it has good applicability.

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