RESEARCH ON THE TREATMENT OF ALUMINUM ALLOY CHEMICAL MILLING WASTEWATER WITH FENTON PROCESS

Huang Zong-liang¹, Li Ru¹, Luo Peng², Gu Jun-li²

(School of Resources and Civil Engineering, Northeastern University, Shenyang 110819, China)

(2873478730@qq.com, liru@mail.neu.edu.cn)

ABSTRACT: The aluminum alloy chemical milling wastewater was treated by Fenton method. The effect of pH value, reaction time, rotational speed, H₂O₂ dosage, Fe²⁺ dosage and the molar ratio between H₂O₂ and Fe²⁺ on the COD removal rate of aluminum alloy chemical milling wastewater were investigated by single factor experiment and orthogonal experiment. The results showed that the optimum operating conditions for Fenton oxidation were as follows: the initial pH value was 3, the rotational speed was 250r/min, the molar ratio of H₂O₂ and Fe²⁺ was 8, the reaction time was 90 min. Under the optimum conditions, the removal rate of the wastewater’s COD is about 72.36%. In the reaction kinetics that aluminum alloy chemical milling wastewater was oxidized and degraded by Fenton method under the optimum conditions, the reaction sequence of the initial COD was 0.8204.

1. INTRODUCTION

Aluminum alloy milling process is a key technology in aircraft manufacturing and the development of Weaponry, widely used in the aluminum alloy surface treatment of aerospace industry, transportation and other industries[1-4]. The main components of aluminum alloying milling wastewater are sodium hydroxide, Na²S, triethanolamine and so on. Traditional methods of treatment include physical methods, chemical methods, and biological methods[5]. As a high-level oxidation technology, Fenton method can produce strong oxidized •OH and be capable of oxidizing and degrading many organic pollutants discretionarily[6-9]. Compared to other traditional water treatment processes, Fenton Advanced Oxidation Process has the advantages of high processing efficiency, simple operation and so on. This study obtained the optimum conditions and the reaction kinetic equation of the oxidative degradation of aluminum alloying milling wastewater by the experiment of the Fenton reagent for aluminum alloying milling wastewater. The experimental results can provide some experimental basis for the treatment of aluminum alloying milling wastewater by Fenton Advanced Oxidation Process.

2. MATERIALS AND METHODS

2.1 Industrial wastewater

Industrial wastewater is collected from an aircraft factory, it was temporarily stored as there is no cost-effective way to deal with it. The COD, pH value of the aluminum alloy chemical milling wastewater were about 40000mg/L, 13.0, respectively. Before the experiment, the aluminum alloy chemical milling wastewater needs to be diluted 50 times.
2.2 Experimental method
Measure 10mL of experimental wastewater and 490mL of deionized water in a beaker, adjust the pH to the desired value, then place the beaker on a magnetic stirrer, adjust the temperature to 25°C and control the speed. Add to the FeSO$_4$•7H$_2$O quantitatively, then add to the H$_2$O$_2$ quantitatively when the FeSO$_4$•7H$_2$O was dissolved. After a certain period of time, close the stirrer and adjust the pH value between 8.5 and 11 with NaOH in order to remove residual H$_2$O$_2$. After standing for 0.5h, the supernatant liquid was used to measure the COD.

2.3 Single factor experiment
The main influencing factors that the aluminum alloy chemical milling wastewater was treated by Fenton method include pH, the concentration of H$_2$O$_2$ and Fe$^{2+}$, reaction time, rotating speed and so on. The influence of various factors on the treatment effect of aluminum alloy milling wastewater was studied by using the control variable method.

2.4 Orthogonal experiment
The four-factor four-level orthogonal experiment was designed based on the optimal parameter range of each factor determined by single factor experiment. The removal rate of COD was obtained by analyzing the optimum process conditions and finally obtaining the optimal combination conditions.

2.5 The apparent kinetics of Fenton oxidation and degradation of aluminum alloy milling wastewater
The relationship between the initial COD concentration and the reaction rate of aluminum alloy milling wastewater was analyzed under the optimal conditions and established the kinetics equation of initial COD concentration and reaction rate.

3. RESULTS AND DISCUSSION

3.1 The single-factor experimental analysis of aluminum alloy milling wastewater by Fenton method

3.1.1 The effects of Al$^{3+}$ on COD removal rate of aluminum alloy milling wastewater
In this study, the experimental water samples contain a large amount of Al$^{3+}$. Before the experiment, the effect of Al$^{3+}$ on the experiment should be investigated firstly. The form of Al$^{3+}$ varies with the concentration of NaOH in the solution, and there are Al(OH)$_4$$^-$$^-$, Al$_2$(OH)$_5$O$_2$$^-$$^-$, NaAl(OH)$_4$, Al(OH)$_6$$^3$$^-$ and other forms of aluminum acid root ions$^{[10-11]}$. The experiment was carried out by adjusting pH value to 7, standing for 1h and settling the flocculation to remove Al$^{3+}$.

Two wastewater samples were used in the experiment which one was not processed and the other Al$^{3+}$ was removed. under the conditions of reaction time 30min, temperature 25°C, pH value 3 and rotational speed 250r/min, 2mL H$_2$O$_2$ and 0.454g FeSO$_4$•7H$_2$O were added to investigate the removal effect of COD (Table 1).

The experimental results show that Al$^{3+}$ has not only no inhibited the treatment of aluminum alloying milling wastewater by Fenton method, but it has certain promotion effect. Due to the large amount of S$^{2-}$ in the aluminum alloy milling wastewater, which can react and generate the precipitation with Fe$^{2+}$, Fe$^{3+}$ and H$_2$O$_2$, so that the efficiency of Fe$^{2+}$, Fe$^{3+}$ and H$_2$O$_2$ is reduced, thus reducing the removal efficiency of COD.

The Al$^{3+}$ in the waste water will be compared with S$^{2-}$ reaction to reduce the S$^{2-}$ in the aluminum alloy milling wastewater, thus improving the removal rate of COD.

Therefore, in the following research process, the aluminum ion of waste water will no longer be removed, and the pH will be adjusted directly to the required values of the experiment.

| Table 1 The influence of Al$^{3+}$ on the COD removal rate |
|---------------------------------|-----------------|----------------|
| Raw water COD | Post-react ion COD | COD removal value |
| COD | rate |

2
3.1.2 The effect of reaction time on COD removal of aluminum alloy milling wastewater. Under the conditions of temperature 25℃, pH value 3, rotational speed 250r/min, the dosage of H₂O₂ and FeSO₄•7H₂O were 1mL, 0.278g, respectively. The reaction time was 10, 20, 30, 40, 50 and 60min, respectively. The change of COD removal rate was shown in Fig 1.

![Fig 1](image1)

It can be seen from Fig. 1 that the removal rate of COD is about 47% within 10 min after the reaction, and the removal rate is only 3% at 1 h. The study of Martinez et al.[12] found that over 90% of COD removed by the Fenton oxidation reaction occurred in the first 10min. After 20min, the change of COD removal rate was smaller and smaller with the extension of time. Due to the immediate reaction of the Fe²⁺ and H₂O₂, the organics in the wastewater can be rapidly oxidized, thus the better treatment can be achieved in a very short time. Then generate Fe³⁺ continue to react with H₂O₂ generated HO₂⁻, although HO₂⁻ also has certain oxidizing, but it is very weak in oxidation compared to •OH, so that the oxidative degradation effect tends to be gentle after 10 min.

3.1.3 The effect of initial pH on COD removal of aluminum alloy milling wastewater. In the reaction time 10min (other conditions are the same as 2.1.2), the pH value was 2,3,4,5,6,7, respectively, it obtained the COD removal rate with the pH changes, as shown in Fig 2.

![Fig 2](image2)
It can be seen from Fig. 2 that the removal rate of COD in wastewater increased first and then decreased with the increase of pH, and the removal rate of COD was the highest at pH value 3, at pH value 7, COD removal rate was significantly reduced. Fe$^{2+}$ and Fe$^{3+}$ easily combine the OH$^{-}$ in the wastewater to form Fe(OH)$_2$ and Fe(OH)$_3$ precipitates when the pH value of the solution is high[13], so that the concentration reduction of Fe$^{2+}$ in the solution is not conducive to the Fenton reaction, thus reduce the amount of •OH generated. In addition, •OH oxidation potential with the increase in pH gradually decreased[14]. When the pH is higher than 4, the self-decomposition of H$_2$O$_2$ formed H$_2$O and O$_2$. Especially in the neutral and alkaline range, due to the lack of sufficient H$^+$, it can also inhibit the decomposition of H$_2$O$_2$ to form •OH[15].

3.1.4 The effect of rotation speed on COD removal of aluminum alloy milling wastewater. In the pH value 3 and the reaction time 10min (other conditions are the same as 2.1.2), the rotation speed was 200, 250, 300, 350, 400, 450r/min, it obtained the COD removal rate with the rotation speed changes, as shown in Fig 3.

![Fig 3 The influence of rotation speed on the COD removal rate](image)

As shown in figure 3, COD removal rate reached a maximum of 47.17% when the speed was 250r/min. When the speed was 450r/min, COD removal rate dropped sharply. The reason may be that when the speed was too fast, it would accelerate the dissolved oxygen in the air, resulting in increasing dissolved oxygen in the wastewater, than dissolved oxygen and Fe$^{2+}$ can react and generate Fe$^{3+}$, resulting in reducing utilization of Fe$^{2+}$.

3.1.5 The effect of H$_2$O$_2$ investment on COD removal of aluminum alloy milling wastewater. In the pH value 3, the reaction time 10min and the rotation speed 250r/min (other conditions are the same as 2.1.2), the rate of H$_2$O$_2$ and Fe$^{2+}$ was 1, 4, 7, 10, 13, 16, it obtained the COD removal rate with the rate of H$_2$O$_2$ and Fe$^{2+}$ changes, as shown in Fig 4.

![Fig 4 The influence of initial dosages of H$_2$O$_2$ on the COD removal rate](image)

It can be seen from Fig.4 that with the increase of H$_2$O$_2$, the removal rate of COD was obviously
rising trend. When the dosage of \( \text{H}_2\text{O}_2 \) was 1mL, namely, the rate of \( \text{H}_2\text{O}_2 \) and \( \text{Fe}^{2+} \) was 10: 1, the removal rate of COD in waste water reached the highest, but when \( \text{H}_2\text{O}_2 \) dosing quantity was more than 1 ml, COD removal rate appeared a downward trend. The reasons that different concentrations of \( \text{H}_2\text{O}_2 \) resulted in significant difference in COD removal rate are as follows.

1). When the amount of \( \text{H}_2\text{O}_2 \) is less, the amount of \( \cdot \text{OH} \) produced is relatively small, and the \( \cdot \text{OH} \) can be fully utilized. With the increase of \( \text{H}_2\text{O}_2 \) dosage, the amount of COD removed will increase.

2). When the dosage of \( \text{H}_2\text{O}_2 \) is more than a certain range, it can be known from the reaction mechanism of Fenton that excessive \( \text{H}_2\text{O}_2 \) reacts with \( \cdot \text{OH} \) that has been generated in the wastewater to produce a weakly oxidized \( \text{HO}_2 \cdot \), This results in both the reduction of \( \cdot \text{OH} \) produced, which also causes the \( \text{H}_2\text{O}_2 \) itself to decompose ineffectively and finally reduces the effect of the reaction \([16]\).

\[
\cdot \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2 \cdot \quad (1)
\]

3.1.6 The effect of \( \text{Fe}^{2+} \) dosage on COD removal of aluminum alloy milling wastewater. In the pH value 3, the reaction time 10min, the rotation speed 250r/min and the dosage of \( \text{H}_2\text{O}_2 \) is 1mL, the rate of \( \text{H}_2\text{O}_2 \) and \( \text{Fe}^{2+} \) was 15, 12, 10, 8, 5, 2, it obtained the COD removal rate with the dosage of \( \text{Fe}^{2+} \) changes, as shown in Fig 5.

![Graph](image_url)

**Fig 5** The influence of initial dosages of \( \text{FeSO}_4 \) on the COD removal rate

As Fig 5 showed that COD removal rate increased first and then decreased with the increase of \( \text{Fe}^{2+} \) dosage. When the rate of \( \text{H}_2\text{O}_2 \) and \( \text{Fe}^{2+} \) was between 8 and 12, COD removal rate reached the maximum value of 51.56 %. In the Fenton reaction system, \( \text{Fe}^{2+} \) mainly plays a catalytic role. Under the acidic condition, with the increase of \( \text{Fe}^{2+} \) dosage, the amount of catalyzed production of \( \cdot \text{OH} \) is more, so that the degradation efficiency of organic matter in wastewater is higher \([17]\). However, when the dosage of \( \text{Fe}^{2+} \) exceeds a certain range, the Fenton reaction equation shows that excessive \( \text{Fe}^{2+} \) reacts with the \( \cdot \text{OH} \) that has been generated to produce \( \text{Fe}^{3+} \), resulting in a decrease in the utilization of \( \cdot \text{OH} \), which degrades the degradation of organic matter in the wastewater.

\[
\text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (2)
\]

In addition, when the dosage of \( \text{Fe}^{2+} \) is too large, the wastewater will produce a lot of iron in the process, increasing the sludge production and processing costs.

3.2 Orthogonal experimental results

| Factors | A | B | C | D | COD removal rate (%) |
|---------|---|---|---|---|----------------------|
| Numbers |   |   |   |   |                      |
| 1       | 4 | 250 | 2 | 30 | 66.77                |
| 2       | 4 | 300 | 3 | 50 | 70.57                |
| 3       | 4 | 350 | 4 | 70 | 66.28                |
| 4       | 4 | 400 | 5 | 90 | 63.25                |
According to the orthogonal experimental results of table 2, the effect of Fenton method on the COD removal rate of aluminum alloying milling wastewater is the rate of $H_2O_2$ and $Fe^{2+}$ > pH > reaction time > rotation speed. The optimal conditions for the treatment of COD of aluminum alloying milling wastewater by Fenton method are that initial pH value was 3, the rate of $H_2O_2$ and $Fe^{2+}$ was 4, the rotation speed was 250 r/min and the reaction time was 90 min.

To analyze the optimal combination of the orthogonal experiment, when the rate of $H_2O_2$ and $Fe^{2+}$ was 4, the average removal rate of COD was 66.72%, compared with the rate of $H_2O_2$ and $Fe^{2+}$ was 8, the average removal rate of COD just increased by 3.89%, but the dosage of $FeSO_4 \cdot 7H_2O$ was increased by 2 times, and the iron in the treated water samples was almost doubled, which greatly increased the sludge treatment cost. After comprehensive consideration, the best combination of the experiment conditions were determined as follows: the initial pH value was 3, the rate of $H_2O_2$ and $Fe^{2+}$ was 8, the rotation speed was 250 r/min and the reaction time was 90 min, under the condition of combination, the COD removal rate reached 72.36%, the best removal effect obtained for this experiment.

3.3 Kinetics of COD in aluminum alloy milling wastewater with Fenton oxidation degradation

In this study, the kinetic relationship between the concentration of reactants and the reaction rate of Fenton treatment of aluminum alloy milling wastewater was investigated. The reaction rate is usually determined by the reaction temperature and the concentration of the reactants. When the reaction temperature is constant, the oxidation degradation rate and the initial COD concentration can be expressed as [18]:

$$V = \left(-\frac{dp}{dt}\right) = KP\alpha$$ (3)

Studying the apparent kinetics of oxidative degradation is to obtain the equation 3, which is the determination of $K$ and $\alpha$ in the equation.

At the temperature was 25 ℃, the rotation speed was 250 r/min, the dosage of $H_2O_2$ was 2mL, the dosage of $FeSO_4 \cdot 7H_2O$ was 0.908g, the initial pH was 3. The initial COD concentration was 566.28, 661.42, 804.44, 848.04mg/L, and the effect of initial COD concentration on the reaction rate of Fenton treatment of aluminum alloying milling wastewater was investigated. When the reaction time was 10, 20, 30, 50, 70, 90 min, respectively, the COD concentration were measured as shown Table 3.

| COD initial (mg/L) | 0   | 10  | 20  | 30  | 50  | 70  | 90  |
|-------------------|-----|-----|-----|-----|-----|-----|-----|
| 566.28            | 233.85 | 220.67 | 198.03 | 180.44 | 166.83 | 159.50 |
| 661.42            | 289.44 | 268.25 | 256.65 | 228.50 | 213.68 | 197.24 |
| 804.44            | 356.62 | 341.71 | 332.11 | 322.16 | 315.56 | 306.47 |
| 848.04            | 391.31 | 379.25 | 369.74 | 334.15 | 308.81 | 303.17 |

Fenton reaction degradation of aluminum alloying milling wastewater is a complex process, COD concentration and reaction time should meet a certain continuous function [19], origin software was...
used to analyze the data in table 3 polynomial fitting (see Fig 6) and obtained the relationship between COD concentration and reaction time curve equation (see Table 4).

Table 4 The fitting results of C-t polynomial in different initial COD concentration

| COD_initial (mg/L) | Polynomial expression | Correlation coefficient | \( R^2 \) |
|-------------------|-----------------------|------------------------|--------|
| 566.28            | \( y = -1.8349x^5 + 4.2321x^4 - 373.74x^3 + 1568x^2 - 3120.5x \) + 2733.6 | 0.9997 |
| 661.42            | \( y = -1.7978x^5 + 4.082x^4 - 356.65x^3 + 1491.7x^2 - 2979.9x \) + 2609.8 | 0.9991 |
| 804.44            | \( y = -1.4995x^5 + 34.123x^4 - 298.23x^3 + 1244.2x^2 - 2481.3x \) + 2163.9 | 0.9998 |
| 848.04            | \( y = -1.416x^5 + 31.964x^4 - 276.66x^3 + 1142.2x^2 - 2255.1x \) + 1924.9 | 0.9988 |

As can be seen from table 4, the polynomial fitting of COD concentration with time change is above 0.998, and the number of COD and the reaction rate constant can be calculated using the experimental data.

The derivative of the above equation at \( t=0 \) is

\[
\left( \frac{dC}{dt} \right)_{t=0} = -3120.5 \quad \left( \frac{dC}{dt} \right)_{t=0} = -2979.9 \quad \left( \frac{dC}{dt} \right)_{t=0} = -2481.3 \quad \left( \frac{dC}{dt} \right)_{t=0} = -2255.1
\]

The positive and negative of the reaction rate doesn't make sense, just stands for the direction of the reaction. The initial reaction rate of different initial COD concentration is shown in table 5.

Table 5 The initial reaction velocity in different initial COD concentration

| COD_initial (mg/L) | lgC_0 | 566.28 | 661.42 | 804.44 | 848.04 |
|-------------------|-------|--------|--------|--------|--------|
| \( \frac{dC}{dt} \)_{t=0} | 2.753 | 2.820 | 2.905 | 2.928 |
| lg(\( \frac{dC}{dt} \)_{t=0}) | 2255.1 | 2481.3 | 2979.9 | 3120.5 |

With \( lgC_0 \) as the abscissa and \( lg(\left( \frac{dC}{dt} \right)_{t=0}) \) as the ordinate (see Fig 7)
The linear equation of the curve can be obtained by Fig 7:

\[ \lg \left( \frac{dC}{dt} \right) = 0.8204 \lg C_0 + 1.0894 \]  

(4)

The correlation coefficient is 0.9918, and the linear fitting is good.

Therefore, the apparent kinetic equation between the initial COD concentration and the reaction rate under the optimum reaction conditions of Fenton oxidative degradation of aluminum alloying milling wastewater is as follows.

\[ V = 12.2857 \times C^{0.8204} \]  

(5)

According to equation 5, the reaction series of aluminum alloying milling wastewater with Fenton method is 0.8204.

4. CONCLUSION

1) The influencing factors of aluminum alloying milling wastewater are as follows: pH value, rotational speed, molar ratio of H$_2$O$_2$ and FeSO$_4$$\cdot$7H$_2$O, reaction time and so on. The order of these factors that affect oxidation degradation of COD by Fenton method is the molar ratio of H$_2$O$_2$ and FeSO$_4$$\cdot$7H$_2$O > pH > reaction time > rotation speed.

2) Based on the single factor experiment, the optimum conditions for the degradation of aluminum alloying milling wastewater by Fenton method were as follows: the initial pH value was 3, the rotational speed was 250r/min, the molar ratio of H$_2$O$_2$ and Fe$^{2+}$ was 8, the reaction time was 90 min. Under the optimum combination conditions, COD removal rate in wastewater can reach 72.36%.

3) The apparent kinetic equation between the initial concentration of COD and the initial reaction rate of the oxidative degradation of aluminum alloying wastewater by Fenton method was as follows.

\[ V = 12.2857 \times C^{0.8204} \]

Through its apparent kinetic analysis, it was found that the initial concentration of COD had a certain effect on the reaction rate and the reaction series was 0.8204.

ACKNOWLEDGEMENT
The research was funded by the Aviation Joint Fund (grant no.2015022004).

REFERENCES
[1] Yu Zhi-lan. Alkali corrosion of aluminum alloy - High precision milling [J]. Light Alloy Fabrication Technology, 1994, 22 (12): 27~28.
[2] O. Çakir. Chemical etching of aluminum [J]. Journal of Materials Processing Technology, 2008, 199 (1-3): 337~340.
[3] Xie Chun-ying, Liu Min, Zhu Kai, etc. Fatigue property of aluminum alloy after chemical milling [J]. Corrosion and Protection, 2008, 29 (4): 185~188.
[4] Yue Jun, Li Na. Fatigue feature of chemical milling on aluminum alloy [J]. China Measurerment and Text, 2009, 35 (4): 115~117.
[5] Zhang Zong-peng. Study on degradation of Benzoic acid wastewater by advanced oxidation...
processes of Fenton [D]. Tianjin University of Science and Technology, 2015.

[6] Li Chang-hai, Jia Dong-mei, Zhang Yan, etc. Optimization of Atrazine wastewater treatment by Fenton oxidation [J]. Environmental Engineering, 2017, 35 (1): 55–58.

[7] Liu Hong, Wang Chuan, Li Xiang-zhong, et al. A novel electro-Fenton process for water treatment: reaction-controlled pH adjustment and performance assessment [J]. Environmental Science & Technology, 2007, 41 (8): 2937–2942.

[8] Neyens E, Baeyens J. A review of classic Fenton’s peroxidation as an advanced oxidation technique [J]. Journal of Hazardous Materials, 2003, 98 (1-3): 33–50.

[9] Kitis M, Adams CD, Daigger GT. The effects of Fenton’s reagent pretreatment on the biodegradability of nonionic surfactants [J]. Water Research, 1999, 33 (11): 2561–2568.

[10] Helen Watling. Spectroscopy of Concentrated Sodium Aluminate Solution[J]. Applied Spectroscopy, 1998, 52 (2) : 250–258.

[11] Wu Xiao-hua, Chen Bin, Li Xiao-bin, etc. Research progress of sodium aluminate soluble liquid crystal decomposition process [J]. Shandong Metallurgy, 2006, 28 (2): 56–60.

[12] Martinez NS, Fernandez JF, Segura XF, et al. Pre-oxidation of an extremely polluted industrial wastewater by the Fenton’s reagent [J]. Journal of Hazardous Materials, 2003, 101 (3): 315–322.

[13] Zhou Wu-yang, Sun Zhi-min, Zhang Chao-sheng. Research on treatment of wastewater containing Cu²⁺ and Dimethyl Phthalate by Fenton oxidation coupled with flocculation [J]. Environmental Engineering, 2016, 34: 378–392.

[14] Qin Le-le. Degradation of refractory organics in Landfill Leachate by advanced oxidation technology based on Fenton research [D]. Beijing Jiaotong University, 2015.

[15] Rivas F, Beltran F, Gimeno O, et al. Fenton-like oxidation of landfill leachate [J]. Environmental Science and Health, 2003, 38 (2): 371–379.

[16] Wang Ping. Study and evaluation on advanced treatment of dye industrial zone’s wastewater by Fenton method [D]. Beijing University of Chemical Technology, 2015.

[17] Wang Fang, Hu Kai-quan, Liu Fu-an, etc. Experiment of advanced treatment for grease wastewater with Fenton reagent [J]. Water Purification Technology, 2015, 34 (4): 47–50.

[18] Li Hong. Study on treatment of PAHs dye wastewater by Fenton advanced oxidation Process [D]. Chong Qing University, 2007.

[19] Wei Zheng, Wang Tao, Du Zhen, etc. Study on oxidation of styrene wastewater by Fenton reagent [J]. Technology and Development of Chemical Industry, 2015, 44 (11): 40–44.