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To cite this article: Ru Li *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **267** 032086

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Pretreatment of aluminium alloy milling wastewater by micro-electrolysis process

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Abstract. The aluminium alloy milling wastewater belongs to high concentration organic alkaline wastewater, the pH value is up to 13-14, and the COD concentration is 3000mg/L-3300mg/L, if direct discharge into water bodies without harmless treatment can seriously endanger the ecological environment and human health. In this study, the micro-electrolysis process was used to pre-treat the aluminium alloy milling wastewater, and the COD removal rate was the indicator. Under the condition that the mass ratio of iron to carbon is 1:2, the dosage of iron is 67g/L, the pH is 3, and the reaction time is 60min, the average removal rate of COD in aluminium alloy milling wastewater can reach 71.34%. The kinetic analysis of the process of pre-treatment of aluminium alloy milling wastewater by micro-electrolysis process is in accordance with the first-order kinetic model. The dynamic equation is: $C_t = C_0 \exp(-3.5762C_0^{-0.6351}t)$.

1. Introduction

Aluminum alloy milling wastewater comes from the chemical milling process in aerospace industry. It will cause some serious health and environmental problems without processing because of its high alkalinity and high organic concentration. Considering the COD of the wastewater is 3000 mg/L-3300 mg/L, it should be pretreated for following process. The micro-electrolysis process was used in the pretreatment in order to decrease the COD significantly in this research. After the iron and activated carbon particles with the particle size of 20-40 mesh were immersed in the wastewater, innumerable primary batteries were formed and an electric field were created in the surrounding space. Under the influence of the electric field, the charged pollutant molecules in wastewater moved to the electrodes with opposite charges. Then, they were degraded into small molecules because of the redox reaction occurred on the surface of the electrodes[1-4].

2. Materials and methods

2.1 Materials

The aluminum alloy milling wastewater was obtained from an aircraft manufacturing enterprise, with pH values of 13-14 and a COD of 3000 mg/L-3300 mg/L. Iron and activated carbon particles were passed through 20-40-mesh sieves. The chemical used in the experiments and analysis were analytical grade products.

2.2 Methods

300 mL of the wastewater and certain quantity of iron and activated carbon particles were stirred on a



six-unit electric agitator (JJ-4A) using 10% H_2SO_4 adjusting the pH values. Samples were taken at intervals to determine COD. The pH values of the solutions were measured by a portable pH meter. Rapid digestion spectrophotometry (HJ/T399-2007) was utilized to determine the COD with the digestion instrument (DRB200) and UV (DR-6000).

3. Results and discussion

3.1 Influencing factors of the pretreatment

3.1.1 Reaction time. Reaction time plays an important role in pretreatment of aluminum alloy milling wastewater by Micro-electrolysis process. With shorter reaction time to arrive the best treatment effect, comes less energy consumption. The effect of reaction time on the removal rate of COD was studied at a pH value of 3 with iron-activated carbon mixture (iron-carbon mass ratio is 1:2, iron dosage is 67 g/L) using 300 r/min electric agitator (Figure 1).

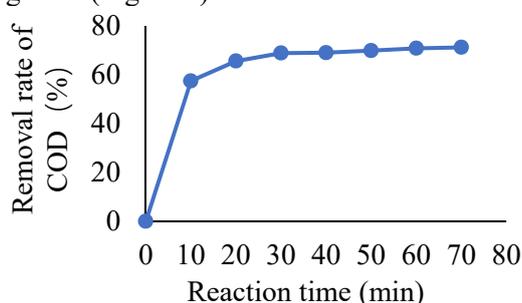


Figure 1. The effect of reaction time on the removal rate of COD.

The removal rate increased significantly at 0-30 min, and it climbed slightly after 30 min and almost no improvement after 60 min. That may be because of the reduction of the iron with increasing reaction time, which caused fewer batteries in the reacting system. What else, with the increase of reaction time, the hydrogen evolution reaction of electrodes consumed a large amount of H^+ , which made the pH of wastewater increased gradually[5]. Therefore, 60 min can be accepted as the optimum reaction time of iron-carbon micro-electrolysis, considering the energy consumption, economic benefit and chromaticity of effluent.

3.1.2 pH. To observe the effect of pH on the removal rate of COD, the experiments were carried out by adding iron- activated carbon mixture (iron-carbon mass ratio is 1:2, iron dosage is 67 g/L), rotating speed of electric agitator was 300 r/min and reaction time was 60 min (figure 2).

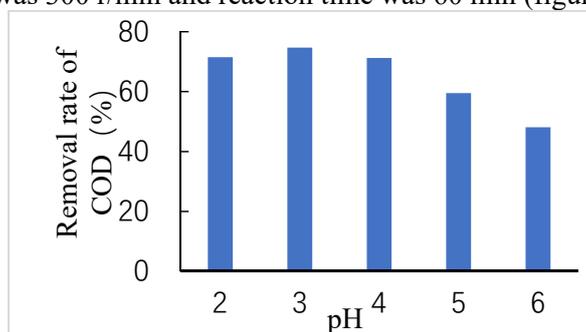


Figure 2. The effect of pH value on the removal rate of COD.

The highest COD removal rate was achieved at a pH value of 3 as given in figure 2. And the treatment effect under acidic condition was better than that under neutral condition. Iron particles corroded faster under acidic conditions. The electrochemical reaction was easier with larger potential difference of primary batteries. The organic pollutants in wastewater can be degraded because of the reducibility of the $[H]$ and Fe^{2+} produced by electrode reaction[6]. The concentration of H^+ in solution

remained low under neutral condition, which caused the decrease of the corrosion rate of iron particles. Accordingly, the potential difference of primary battery decreased. Then the COD removal rate declined, because the electrochemical reaction was difficult to carry out.

3.1.3 Iron dosage. The effect of iron dosage on the removal rate of COD was investigated at a pH value of 3. Rotating speed of electric agitator was 300 r/min and reaction time was 60 min (figure 3).

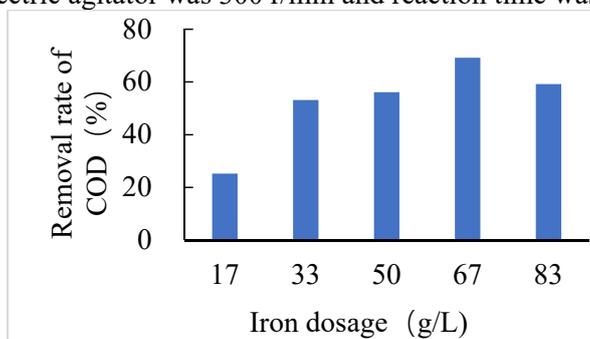


Figure 3. The effect of iron dosage on the removal rate of COD.

The removal rate of COD increased significantly when the iron dosage increased from 17 g/L to 67 g/L. Then, it declined slightly with the iron dosage of 83 g/L. With more iron dosage, came more primary batteries and larger potential difference on the electrodes. When iron particles were excessive, they began to react with acidic wastewater, which consumed H^+ in water[7]. Then, the removal rate of COD decreased with higher pH values and less electrode reaction.

3.1.4 Iron-carbon mass ratio. The effect of iron-carbon mass ratio on the removal rate of COD was studied at a pH value of 3 with 67 g/L iron. Rotating speed of electric agitator was 300 r/min and reaction time was 60 min (figure 4).

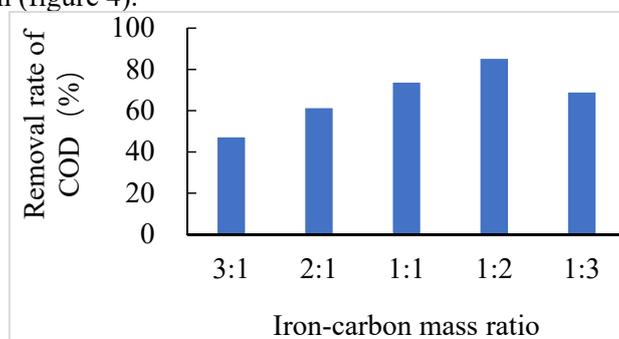


Figure 4. The effect of iron-carbon mass ratio on the removal rate of COD.

The highest removal rate of 85.05% was achieved when the iron-carbon mass ratio is 1:2. On the one hand, too much iron particles led to excessive formation rate of Fe^{2+} in solution. $\cdot OH$ was reacted with Fe^{2+} , which caused the decrease of the removal rate of COD[8]. On the other hand, iron particles were surrounded by excessive activated carbon. The mass transfer of iron particles and solution were depressed as well as the electrode reaction.

3.2 orthogonal experiment

L9(3⁴) orthogonal experiment with four factors and three levels was carried out, with iron-carbon mass ratio, iron dosage, influent pH values and reaction time as variables.

Table 1. The results of orthogonal experiments.

Seque-nce	A Iron-carbon mass ratio	B Iron dosage(g/L)	C pH values	D Reaction time(min)	Removal rate of COD(%)
1	1: 1	50	2	50	62.43
2	1: 1	67	3	60	67.86

3	1: 1	83	4	70	68.49
4	1: 2	50	3	70	72.11
5	1: 2	67	4	50	69.98
6	1: 2	83	2	60	71.57
7	2: 1	50	4	60	55.38
8	2: 1	67	2	70	67.64
9	2: 1	83	3	50	63.49

According to the range of each factors, the order of influencing COD removal rate was as follows: iron-carbon mass ratio > iron dosage > reaction time > influent pH values. Iron-carbon mass ratio of 1:2, iron dosage of 67 g/L, a pH value of 3 and reaction time of 70 min can be accepted as the optimum condition. The reaction time would be 60 min, considering the effect of reaction time on the pH value of wastewater and the convenience of timing in practical engineering.

Table 2. The variance analysis of orthogonal experiments.

Factors	A	B	C	D
k ₁	198.78	189.92	201.64	195.9
k ₂	213.66	205.48	203.46	194.81
k ₃	186.51	203.55	193.85	208.24
K ₁ ^a	66.26	63.31	67.21	65.30
K ₂ ^a	71.22	68.49	67.82	64.94
K ₃ ^a	62.17	67.85	64.62	69.41
R ^b	9.05	5.19	3.20	4.48

^a Average removal rate at x level

^b Range

3.3 Kinetic analysis

In electrochemical process, it is direct oxidation reaction that mainly occurs on the surface of electrodes[9]. The variation of COD with time changing can be simplified to the following formula: $-dC_a / dt = kC_a^n$. The correlation coefficients of different reaction orders were calculated according to zero order, first order, second order and third order reaction kinetics equations, respectively (table 3).

Table 3. The relation of COD concentration and reaction time.

Reaction time (min)	C _t	$-\ln(C_t/C_0)$	$(1/C_t - 1/C_0)$	$(1/C_t^2 - 1/C_0^2)/2$
0	3303.18	0	0	0
10	2476.78	0.2879	0.0001010	3.56817E-08
20	2074.74	0.4650	0.0001792	7.03309E-08
30	1660.4	0.6878	0.0002995	1.35536E-07
40	1300.59	0.9321	0.0004661	2.49764E-07
50	1144	1.0604	0.0005714	3.36223E-07
60	967.38	1.2280	0.0007310	4.88463E-07
R ²	0.9347	0.9907	0.9894	0.9422

As seen in table 3, the linear correlation was the best when the first-order reaction kinetics equation was used to fit the reaction process of micro-electrolysis in the treatment of aluminum alloy milling wastewater. Kinetic equation is $C_t = C_0 \exp(-kt)$. To observe the relationship of reaction rate constant k and C₀, the experiments were carried out under the optimum conditions and the raw water was diluted to different concentrations (table 4). From table 4 we can calculate that $k = 3.5762C_0^{-0.6351}$. $C_t = C_0 \exp(-3.5762C_0^{-0.6351}t)$ would be the kinetic equation.

Table 4. The results of experiments at different COD concentrations.

Index	COD concentrations (mg/L)
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Raw water	2909.24	3303.18	3748.25	4395.7	4990.19
Effluent water	737.76	967.38	1198	1502.95	1931.01
lnk	-3.7781	-3.8889	-3.9628	-4.0237	-4.1462
lnC ₀	7.9756	8.1026	8.229	8.3884	8.5152

4. Conclusion

The optimum experimental conditions have been investigated through single factor experiments and orthogonal experiments as follows: iron-carbon mass ratio of 1:2, iron dosage of 67 g/L, a pH value of 3 and reaction time of 60 min. Numerous tiny primary batteries were formed by particles of iron and activated carbon in the wastewater. The pollutants were removed by redox reaction occurred on the surface of the electrodes and coagulation of iron ions in the wastewater. Kinetics analysis of the reaction process of micro-electrolysis for treating aluminum alloy milling wastewater was carried out. The process conformed to the first-order kinetics model with reaction rate constant $k=3.5762C_0^{-0.6351}$ and kinetic equation $C_t=C_0 \exp(-3.5762C_0^{-0.6351}t)$. Compared with the experimental data, it is proved that the equation has good applicability.

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