Pretreatment of Chemical Cleaning Wastewater by Microelectrolysis Process

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Abstract

Ferric-carbon electrolysis technology was evaluated for the pre-treatment chemical cleaning wastewater. The volume ratio of Fe and C was set to 1:1, and the effects of pH value, reaction time and aeration rate on pollutant removal efficiency were investigated. The results show that at pH=3.0, reaction time was 60 min and the aeration rate was 1:1. The removal efficiency of COD was 66.4\% and the removal efficiency of oil was 47.8\%. The biodegradability was greatly improved, and BOD5/COD of the pretreated wastewater increased to 0.32 from 0.12. It is demonstrated that Ferric-carbon electrolysis technology can effectively pretreat chemical cleaning wastewater.

Keywords: Chemical cleaning wastewater; Ferric-carbon microelectrolysis; Biodegradability

Oily wastewater of high concentration, especially oily chemical cleaning waste of high concentration, comes from the processing of metallic and non-metallic surfaces. The oily wastewater is organic electroplating wastewater (also known as "pre-plating wastewater"). It is different from the conventional organic wastewater in two aspects: first, the wastewater contains a lot of organic polymers, such as surface active agent, and its biodegradability is poor\cite{1}; second, the wastewater containing high salt, together with a high degree of chemical cleaning agent dispersion, is one of the refractory organic wastewater in metal processing industry. Selecting an appropriate preprocessing method is to determine the effect of subsequent biochemical treatment.

Microelectrolysis, known as inner electrolysis and zero-valent iron method\cite{2,3}, has been developed in recent 30 years, and sets electrochemistry, oxidation-reduction, physical adsorption, and flocculation and other functions in one. When used for treating high concentration organic wastewater, the performance of microelectrolysis is good in refractory organics oxidation, decolorization, enhanced flocculation, and improving biodegradability. In particular, new non-board electrolysis fillers is successfully developed andapplied, to overcome the bottleneck of the constrain of traditional large-scale use of iron and carbon fillers. The new non-board electrolysis fillers have been widely used in nitroaromatic pesticides\cite{4}, acid mine drainage\cite{5}, stormwater\cite{6} and other wastewater treatment. In this paper,

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oily chemical cleaning wastewater of high concentration was treated by micro-electrolysis. The effect of the process in treating cleaning wastewater is discussed to optimize parameters, providing a reference for engineering applications.

1. Methods and Materials

1.1. Materials

Characteristics of the chemical cleaning wastewater used in the study is shown in table 1.

Table 1. Characteristics of chemical cleaning wastewater

| Index | COD/mg·L⁻¹ | BOD₅/mg·L⁻¹ | Oil/mg·L⁻¹ | pH |
|-------|------------|-------------|------------|----|
| Value | 20368      | 2445        | 320        | 11.3 |

Experimental setup is given in Fig. 1. The device size is φ80×120 mm, and the effective volume is 500 mL. Porous aeration tube was used. The structure of electrolysis fillers is porous alloy, which are sintered with the active iron, carbon, pore agent and solid metal catalysts. The volume ratio of active iron and carbon is 1:1. Packing density of fillers is 1000-1100kg/m³, and single packing size is φ65×50 mm. The shape is honeycomb-like and the porosity is 30%.

![Fig.1. Multiple electrolysis reaction device: 1. pH meter; 2. electrolysis fillers; 3. reactor; 4. porous support plate; and 5. aeration head](image)

1.2. Methods

The pH value of wastewater was adjusted to 2.0, 2.5, 3.5, 4.5 and 5.0, and then electrolytic fillers were added into the wastewater. The volume ratio of fillers and raw water was 1:3. The bottom aeration was carried out by mechanical way. The impact of air to water ratio of 0.5:1, 1:1, 3:1 and 5:1 on treatment effect was determined. Sampling was carried out at 30, 45, 60, 90 and 120 min intervals after the reaction began. The pH value of samples were adjusted to 7~8. 200 mg/L poly aluminum chloride(PAC) and 5 mg/L anionic polyacrylamide were added into the samples with certain pH successively, while stirring. Finally, the samples were settled for 30 min and the supernatants were analyzed.

1.3. Analysis

Analyses of chemical cleaning wastewater characteristics, including COD, BOD5 and pH were conducted. COD was determined by potassium dichromate method. BOD5 was determined by dilution and inoculation method. pH value was determined by pH meter.
2. Results and Discussion

2.1. Effect of the raw water pH on removal

Electrolysis occurs hydrogen evolution reaction mainly in the acidic condition. It is generally believed that reaction intensity keeps higher at low acidity. However, for the specific water quality and various organic pollutants, there exists an optimal pH range. The effect of the raw water pH on COD removal is shown in Fig. 2.

Fig. 2 shows that the COD removal efficiency is higher at low pH value. Under the partial acidic condition, [Fe] and [H] have strong reducing capacity and can restore some organic matters of the oxidation state into the reduced state, but more acid is required to adjust. When the pH value is between 2.5 to 3.5, COD removal efficiency decreases from 58% to 52%. And COD removal efficiency decreases obviously when the pH value exceeds 3.5. It can clearly be seen that it is appropriate to control pH between 2.5 and 3.0.

2.2. Effect of reaction time on removal

Reaction time is an important factor in treatment effect. It can be seen from Fig. 3 that COD removal efficiency increases with the increasing reaction time, and at 60 min the removal efficiency of COD reaches the maximums, 63%. But 60 min later, with the increasing reaction time, the removal efficiency declines. This is probably because the reaction time is too long, a large amount of ferrous ions affect the anodic dissolution of iron. In addition, the length of time determines the size and investment of the micro-electrolysis reactor. Therefore, the reaction time for micro-electrolysis treatment was determined to be 60 min for further experiment.
2.3. Effect of aeration rate on removal

Aeration can improve the mass transferring condition of micro-electrolysis process and the dissolved oxygen can participate in micro-electrolysis reaction to accelerate electrochemical corrosion.

![Fig. 4. The effect of aeration rate on COD removal (pH=3.0; reaction time=60 min)](image)

It can be seen from Fig. 4, when the electrolysis reaction conditions without aeration, the treatment is poor. COD removal efficiency is 40%. After aeration, COD removal significantly increases. When the air to water ratio is 1:1, COD removal efficiency reaches 57.3%. With the increasing aeration, the increasing trend of COD removal efficiency slows. Taking into account that the increase of aeration would increase the power consumption, the aeration rate for micro-electrolysis treatment was determined to be 1:1.

2.4. Effect of continuous treatment

In summary, the conditions of micro-electrolysis are air to water ratio of 1:1, the raw water pH = 3.0 and reaction time of 60 min. Table 2. shows the changes of chemical cleaning wastewater quality after treating. After treatment, COD is reduced to 6850 mg/L from 20368 mg/L, and the COD removal efficiency is 66.4%. BOD5/COD is increased to 0.32 from 0.12. Oil is reduced to 167 mg/L from 320 mg/L, and the oil removal efficiency is 47.8%.

Table 2. The treatment of chemical cleaning wastewater

| Index                     | pH  | COD/ mg·L⁻¹ | BOD5/ mg·L⁻¹ | BOD5/COD | Oil/mg·L⁻¹ |
|---------------------------|-----|-------------|--------------|----------|------------|
| Raw water quality         | 11.3| 20368       | 2445         | 0.12     | 320        |
| Water after the reaction  | 7.2 | 6850        | 2219         | 0.32     | 167        |
| Removal efficiency /%     | -   | 66.4        | 9.2          | -        | 47.8       |

3. Conclusions

The results show that it is feasible to use honeycomb-like fillers to treat chemical cleaning wastewater in micro-electrolysis process. The fillers are sintered with iron and carbon whose volume ratio is 1:1. After reaction time of 60 min, at pH=3.0, COD removal efficiency of oily cleaning wastewater can reach more than 65% and oil removal efficiency can reach more than 45%. Biodegradability of wastewater is greatly improved and BOD5/COD value increases from 0.12 to 0.32 after treatment. It provides the basis for the biochemical treatment of oily cleaning waste water with high concentration.
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