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Experimental study on micro-electrolysis technology for pharmaceutical wastewater treatment

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Abstract: Experiments were conducted to study the role of micro-electrolysis in removing chromaticity and COD and improving the biodegradability of pharmaceutical wastewater. The results showed that the use of micro-electrolysis technology could remove more than 90% of chromaticity and more than 50% of COD and greatly improved the biodegradability of pharmaceutical wastewater. Lower initial pH could be advantageous to the removal of chromaticity. A retention time of 30 minutes was recommended for the process design of micro-electrolysis.

Key words: Micro-electrolysis, Pharmaceutical wastewater, Chromaticity, Biodegradability, Enviromental engineering

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INTRODUCTION

Recently, more and more attention has been paid to electrochemical methods of industrial wastewater treatment, among which electrolysis has been the most frequently used unit process due to its rapid reaction rate, high efficiency and reduced sludge. However, the high consumption of electricity limits its further application and leads to the development of micro-electrolysis in wastewater treatment (Han et al., 1987).

Many electrolysis devices that make use of a new kind of material for industrial wastewater treatment were reported in the World Patent Index (WPI). The promising method makes use of the domino effect of electric field, reaction of electro-coagulation and reaction of redox at the surface of the material (Yang et al., 1996; Tang et al., 1998). Essentially, when two metals with different electrode potentials are joined to each other and immersed in an electrolyte solution, a primary battery is formed and an electric field produced. The colloid particles and impurities in wastewater can be agglomerated into larger grains and removed by their sedimentation at the electrodes (Xiao et al., 2000; Tang et al., 1998).

Iron-carbon as a primary battery has been one of the most effective micro-electrolysis methods (Quan et al., 1989), among which the iron scrap was typically studied mainly for industrial wastewater treatment with the following advantages:

1. Instead of industrial material, waste iron scraps can be used as iron-carbon grains to be cost-efficient, which is a waste minimization process (Zhang, 2000).

2. The primary batteries can be formed and work by themselves with no need of power supply and addition of chemical agents. The cost of treating 1 m^3 wastewater using micro-electrolysis is about 0.04 $, considerably lower than that by other methods. Compared with electrolysis, micro-electrolysis is much more economical, environment-friendly and feasible; and is a promising technique with great potential for application.

3. This method can be applied to a large variety of wastewater from several types of industry.

For the last 10 years, iron scrap or powder has reportedly been used to treat all kinds of industrial wastewater.

METHODS AND MATERIALS

1. Methods

(1) Adjust the pH of wastewater.

(2) Treatment of iron grains: Immerse 80g of iron-carbon grains in 800 mL low concentra-

tion acid for 30 minutes to activate them. Discard the waste acid and wash the grains (with distilled water) to neutral in the beaker.

(3) Pour 500 mL wastewater into the beaker and stir continuously. Sample at 5, 10, 20, 30, 45, 60, 90 and 120 minutes intervals after the reaction began and store in small beakers.

(4) Filter the samples to get clear solutions; determine the pH of the solutions.

(5) Add solution of NaOH into the samples; after formation of flocculi, remove them by sedimentation, and then determine the COD and chromaticity of the samples.

(6) Repeat steps 1 – 5 for wastewater at another pH value.

Fig. 1 shows a schematic drawing of the experiment.

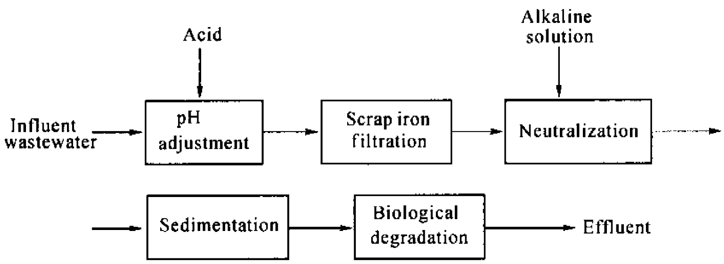

Fig. 1 Experimental flow diagram

2. Wastewater

Characteristics of wastewater used in this study is shown in Table 1.

Table 1 Characteristics of wastewater influents

Pharmaceutical Wastewater	Initial pH	CODcr (mg/L)	Chromaticity
No. 1	2.36	2550	5000
	5.07	2550	5000
	9.08	2550	5000
No. 2	2.33	25000	5000
	5.72	25000	5000
	8.78	25000	5000

RESULTS AND DISCUSSIONS

1. Effect of initial pH on chromaticity removal

Figs. 2 and 3 show that the removal efficiency of chromaticity was up to 90%. The experimental results showed that initial pH and retention time are two important factors that affect the removal of the chromaticity by micro-electrolysis. Increasing the time of reaction can accebrate the removal of the chromaticity, but also increase the cost of equipment investment. An appropriate retention time should be chosen on the basis of practical considerations; 30 – 40 minutes were recommended in the present study.

It is known that in electrode reaction, the

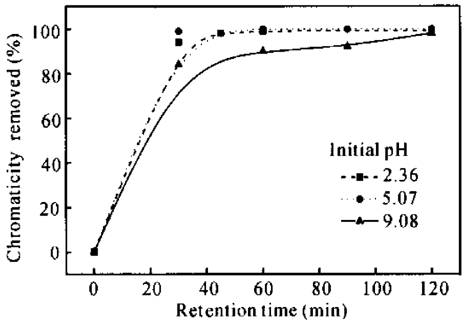

Fig. 2 The removal of chromaticity for No. 1 pharmaceutical wastewater

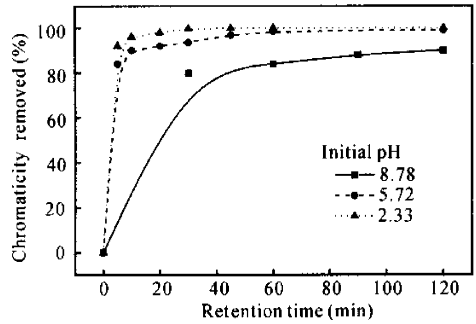

Fig. 3 The removal of chromaticity for No. 2 pharmaceutical wastewater

normal electrode potential of oxygen is higher in acid medium than in neutral medium (Yang et al., 1985). Therefore, reducing the pH of wastewater can accordingly increase the electrode potential of oxygen hence, the potential difference of the micro-battery, and thus accelerate the electrode reaction. Figs. 2 and 3 show that the removal of chromaticity decreases with increasing initial pH. The fact that wastewater has higher chromaticity removal efficiency in acid medium than in basic medium indicates that H^+ ions play an important role in chromaticity removal, possibly by a mechanism of deoxidation in which H^+ ions react with the organic compound of pollutants in wastewater and cause the chain rupture of chromophoric or anxochromic groups from the organic compound molecules.

2. Change of pH with reaction time at different initial pH of pharmaceutical wastewater

Figs. 4 − 6 show the change of pH with retention time in acid, neutral and alkaline conditions, respectively.

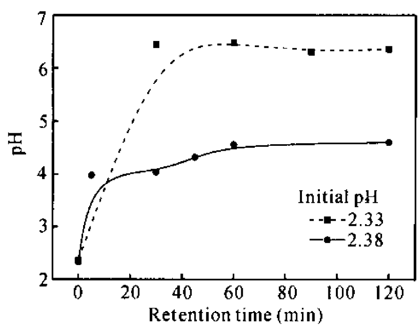

Fig. 4 The change of pH of No. 2 pharmaceutical wastewater with retention time in acid condition

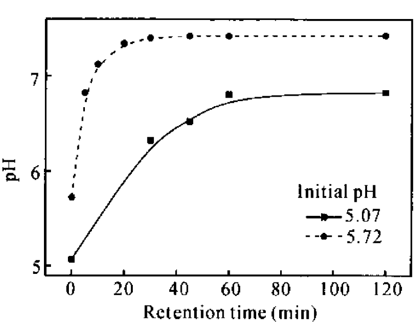

Fig.5 The change of pH of No.2 pharmaceutical wastewater with retention time in neutral condition

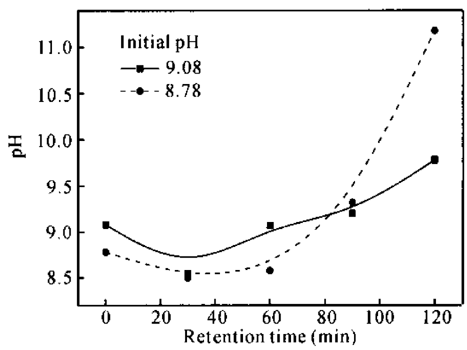

Fig.6 The change of pH of No.2 pharmaceutical wastewater with retention time in basic condition

Scrap iron, as a kind of iron-carbon alloy, can form millions of iron-carbon primary batteries in electrolyte solutions. The anode reaction is: $Fe - 2e = Fe^{2+}$; at the same time, Fe^{2+} ions are oxidized into Fe^{3+} ions by dissolved O_2 in the solution. At the cathode, H^+ ions react with dissolved organic compounds. And some other reactions also take place in the solution: (1) $O_2 + 2H_2O = 4OH^-$ and (2) $Fe^{3+} + 3OH^- = Fe(OH)_3$, which produces large amount of $Fe(OH)_3$ flocculi; (3) $Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$, which decreases solution pH. In acid or neutral conditions where high concentration H^+ ions are present, with the consumption of H^+ ions in the course of reaction, the wastewater pH tends to increase with time. In basic condition wherein OH^- ions are present at high concentration, the existence of reaction (2) can result in decrease of wastewater pH at the initial stage of reaction; as time goes on, however, the reaction (1) becomes the dominating one which can produce OH^- ions and cause the pH of the wastewater to rise in the final stage of reaction.

3. Effect of initial pH on COD removal

The initial pH and the retention time are two important factors affecting the efficiency of the COD removal. Fig. 7 shows that the efficiency of the wastewater COD removal varies with retention time at different initial pH. It is known that the attack of H^+ ions would cause the organic compounds to be deoxygenated and result in a rising wastewater COD. But the OH^- ions produced by the reaction (1) would combine with Fe^{3+} ions to form $Fe(OH)_3$, which can adsorb organic compound molecules and result in the decrease of COD. So the wastewater COD changes as a result of combined effects. Besides these, the sedimentation by electrophoresis can also remove part of the COD (Yang, 1992). That is the reason why neutral or alkaline condition is helpful to COD removal, which was observed in experiments.

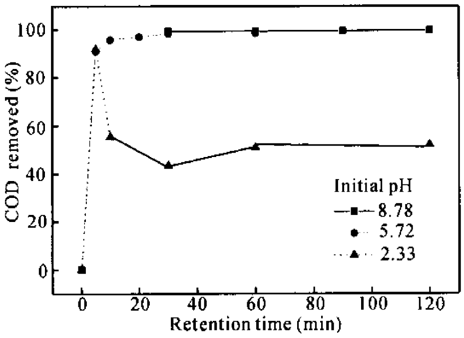

Fig. 7 The COD removal of No. 2 pharmaceutical wastewater with retention time at different initial pH

4. Biodegradability of pharmaceutical wastewater after micro-electrolysis

Aeration tests were conducted to study the biodegradability of pharmaceutical wastewater treated by micro-electrolysis. The change of COD and BOD/COD of pharmaceutical wastewater into and out of the aeration basin of after 24 hours retention time are shown in Tables 2 and 3.

Table 2 The change of COD after 24-hour aeration

Influent(mg/L)	Effluent (mg/L)
13876	9654
789	456
389	145

Table 3 The change of BOD/COD after 24-hour aeration

Influent BOD/COD	Effluent BOD/COD
0.27	0.42
0.29	0.45
0.29	0.44

Results showed that half of the COD can be removed by the 24-hour aeration for the wastewater treated by micro-electrolysis and that the value of BOD/COD increases obviously, which means that the biodegradability of the wastewater was greatly improved by micro-electrolysis. It can be explained that in the treatment with iron-carbon grains, the chain rupture of chromophores takes place and the big molecules of refractory products and intermediates are broken into more easily biodegradable small ones (Wei, 2001). With all those reactions occurring in the micro-electrolysis process, the BOD and the biodegradability of pharmaceutical wastewater improve greatly.

CONCLUSIONS

Iron-carbon grains treatment can remove more than 90% of chromaticity and more than 50% of COD from pharmaceutical wastewater. The efficiency of this method is found to be sensitive to the initial pH of wastewater. Lower initial pH will result in an increased chromaticity removal efficiency and decreased COD removal efficiency.

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