

Experimental Study on the Treatment of 1, 4 butanediol Mixed Wastewater by Ferro-carbon Micro-electrolysis

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Abstract. The mixed wastewater of 1, 4 butanediol was tested with iron filings and carbon powder as catalyst by aeration to provide oxygen. The effects of carbon powder, pH value and reaction time on wastewater treatment were studied. The optimal experimental condition was that the mesh number of activated carbons was 20, the pH value was 5, the reaction time was 30min, and the Chemical Oxygen Demand (COD) removal efficiency reached 36.2%. At the same time, The response surface method was used to analyze and optimize the experimental results, and the relation formula of each influencing factor on removal efficiency was established, and the order of influence degree of each factor on removal efficiency (pH > activated carbon mesh number > reaction time) was obtained, in which pH had the greatest influence on the treatment rate of ferro-carbon micro-electrolysis treatment of 1, 4-butanediol wastewater.

1 Introduction

1, 4 butanediol is an important organic chemical raw material, which is widely used in pharmaceutical chemical textile paper cars and daily chemical industry [5]. At present, the commonly used production technology is alkyl aldehyde method, and the products are 1,4-butanediol (THF), 1,4butyne glycol (BYD), polytetrahydrofuran (PTMEG) etc. THF and PTMEG is a kind of toxic organic compounds, from structural analysis belongs to refractory material, is great harm to human health [1][2].

Ferro-carbon micro-electrolysis used the metal corrosion principle method to conduct electrolytic treatment of the waste water, by using the self-generated 1.2V potential difference of the micro-electrolytic material filled in the waste water without power, and achieve the purpose of degrading organic pollutants. Under acidic conditions, it is conducive to the micro-electrolysis reaction, which can speed up the reaction rate. The oxidation reduction reaction of dissolved oxygen and Fe^{2+} in wastewater will destroy the molecular structure of some organic substances. The Fe^{3+} will flocculate the organic substances in waste water and further remove the pollutants [3]. Activated carbon surface contains a large number of acidic or alkaline groups, which have adsorption capacity and

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catalytic effect. When there is O_2 or hydrogen peroxide (H_2O_2) in wastewater, the pollutants in wastewater are catalyzed and oxidized [4].

In this study, 1, 4 butanediol mixed wastewater was taken as the research object, air was taken as the oxidant, and the effects factors such as pH, reaction time and activated carbon mesh number were studied. The experimental results indicated that the activated carbon mesh number was 20, pH value was 5, reaction time was 30min, and the COD removal efficiency reached 36.2%, which provided the fundamental researches for the Ferro-carbon micro-electrolytic treatment technology of 1, 4-butanediol mixed wastewater. Response Surface Methodology (RSM) was used to analyze and optimize the experimental results, and a quadratic polynomial mathematical model was established for the relationship between COD removal efficiency and various factors, and effect of the different factors on COD removal efficiency was analyzed.

2 Materials and methods

2.1 Materials

The wastewater comes from BDO and PTMEG production workshops of a chemical enterprise in China. The wastewater quality was as follows: COD 6000~12000 $mg L^{-1}$, biochemical oxygen demand (BOD_5) 596~1800 $mg L^{-1}$, B/C 0.083~0.11, pH 6~9, salt concentration 0.06 wt%. The main effluent discharge and pollutant concentration are shown in Table 1.

Table 1. Sewage discharge and pollution characteristics of a chemical enterprise in northwest china.

No	Parameter	Flow / $m^3 h^{-1}$	Concentration / $mg L^{-1}$	Toxicity	Biodegradation	Pretreatment
1	BDO	20	1800	N	Easy	N
2	BYD	15	200	N	Difficult	Y
3	HCHO	10	3600	Y	Bacteriostatic	Y
4	PT/THF	8	3700	Y	Bacteriostatic	Y

2.2 Test instrument

The test instruments mainly include a small Ferro-carbon reactor and pH meter and COD meter and etc.

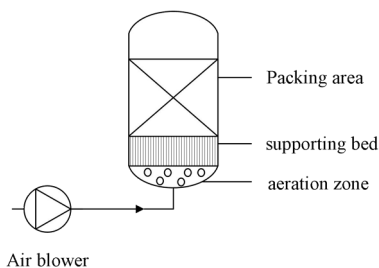


Fig. 1. Structure of the Ferro-carbon reactor

2.3 Methods

- (1) Rinse the activated carbon with clean water before use, soak it in the waste water, and dry it.
- (2) Put the activated carbon and iron shavings in a self-made aeration device, which is full of waste water, then in the reaction.
- (3) Adjust the pH of the reaction wastewater to pH near neutrally, and test the COD of the supernatant after filtration.

3 Results and Discussion

3.1 Results

3.1.1 Effect of activated carbon mesh number on COD removal efficiency

When the Fe-C mass ratio was 1:1, the pH was 4 and the reaction time was 50 min, changed the mesh number of activated carbons, the removal efficiency of COD in wastewater after the reaction was shown in Table 2.

Table 2. Influence of activated carbon mesh number on COD removal efficiency

Activated carbon mesh	8	15	20	30
Removal efficiency /%	20.8	24.4	34.8	23.9

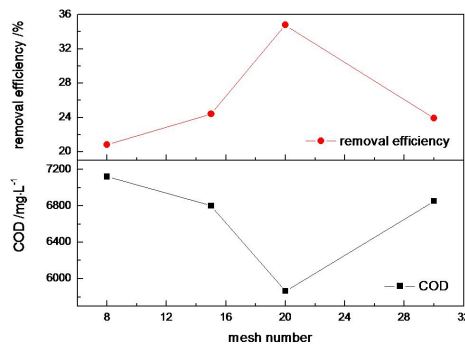


Fig. 2. Influence of activated carbon number on COD removal efficiency

3.1.2 Effect of pH on COD removal efficiency

As shown in Table 3, when the Fe-C mass ratio was 1:1, the pH was 4 and the reaction time was 50min. The removal efficiency of COD in waste water was changed by changing the pH.

Table 3. Effect of pH on COD removal efficiency

pH	3	4	5	6	7	8
Removal efficiency /%	22.4	28.8	36.2	24.5	21.5	20.8

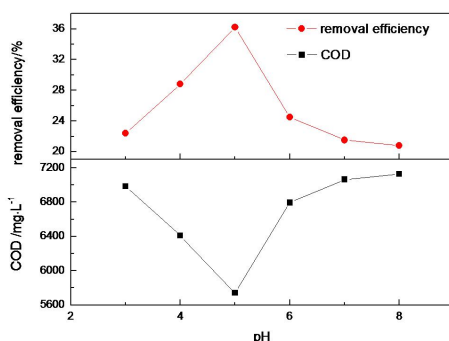


Fig. 3. Influence of pH on COD removal efficiency

As shown in Fig. 3, with the increase of pH, COD removal first increased and then decreased. When the pH was 5, the removal efficiency reached up to 36.2%. When the pH was low, the treatment efficiency was generally better than the alkaline conditions. However, when pH was too low, iron dissolved a large amount of Fe^{3+} and Fe^{3+} causes flocculation and precipitation of organics, which is easy to cause packing blockage, which was not conducive to the formation of the original battery and the removal of COD. On the other hand, when pH was alkaline, H^+ concentration was low, which was also not conducive to the formation of the original battery and reduced the COD removal efficiency on the effect of Ferro-carbon micro-electrolysis.

3.1.3 Effect of reaction time on COD removal efficiency

When the Fe-C mass ratio was 1:1 and the pH value was 5 and the activated carbon number was 20, changes the reaction time, the removal efficiency of COD in the wastewater after the reaction was shown in Table 4.

Table 4. Effect of reaction time on COD removal efficiency

Reaction time / min	10	20	30	40	50
Removal efficiency / %	25	26	33.5	34.6	35.2

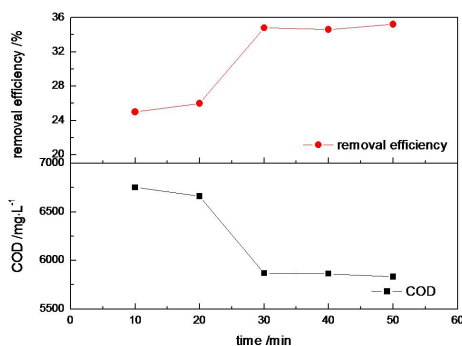


Fig. 4. Reaction time of pH on COD removal efficiency

Fig. 4 shows that, with the extension of reaction time, the removal efficiency of COD gradually increases. When the reaction time was 30min, the removal efficiency was 33.5%.

When the reaction time exceeded 30min, the removal efficiency of COD increased slowly with the increase of reaction time, and remains basically unchanged. The possible mechanism is that the oxidative effect of Ferro-carbon microcells is close to the maximum treatment capacity of pollutant degradation. Meanwhile, the adsorption and catalytic oxidation of activated carbon to COD achieves the dynamic balance under certain pollutant concentration and aeration conditions.

3.2 Discussion

Response Surface Methodology (RSM) is a mathematical statistical method for optimization of multi-factor system, which has been widely used in optimization of various waste water treatment processes, is a reliable and simple statistical tool^{[7][8]}.

In this study, RSM was used to analyze and optimize the main influencing factors, which includes the mesh number of activated carbons, pH and the reaction time, in the process of Ferro-carbon micro-electrolysis treatment of 1, 4-butanediol mixed wastewater.

A quadratic polynomial was established for the relationship between the response R1 (COD removal efficiency) and each parameter (reaction time A, pH is B, and the mesh number of activated carbon is C), which is coded as follows:

$$R1=30.6+0.077A-1.91B+0.19C+0.04AB+0.02AC+0.08BC \tag{1}$$

The A, B and C are encoding values of the response parameters, the factors before the encoding values represent the influence direction and influence the degree of the parameters ^[7]. According to the formula:

$$R1=30.6+0.077A-1.91B+0.19C+0.04AB+0.02AC+0.08BC$$

The study of Ferro-carbon micro-electrolysis conducts that the number of time and activated carbon has a positive effect on the response R1, while the pH has a negative effect on the response volume R1. The order of influence degree was: pH > the mesh number of activated carbons > reaction time, and pH had the greatest influence on the treatment efficiency of 1, 4 butanediol wastewater by Ferro-carbon micro-electrolysis.

Table 5. Experimental results of 1,4butanediol wastewater

NO	A time/ min	B pH	C mesh	Removal efficiency / %
1	50	7	30	16
2	50	3	8	28.9
3	50	3	30	34.6
4	10	7	30	26
5	10	7	8	21
6	10	3	30	28
7	50	7	8	24
8	10	3	8	26

3.2.1 Fitting optimization of pH with reaction time

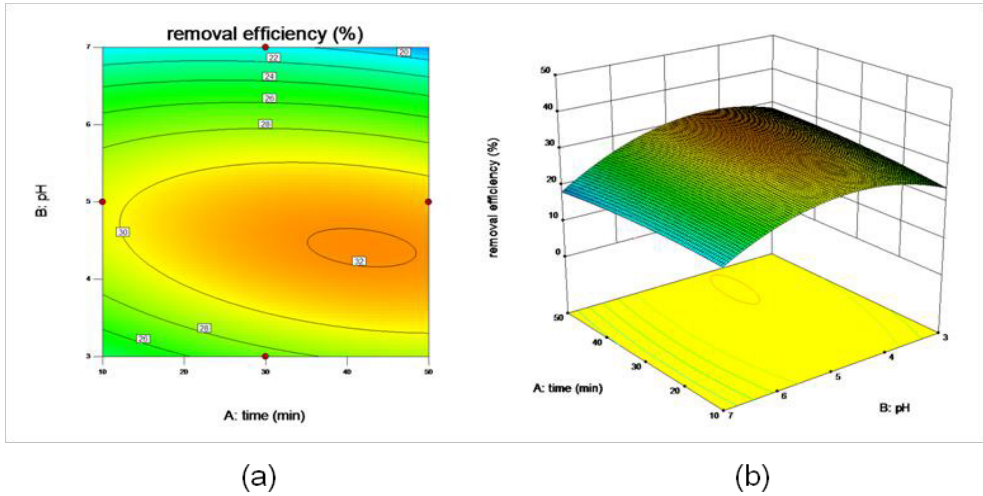


Fig. 5. Effect of reaction time and pH on COD removal efficiency (a) contour map (b) response surface map

Fig. 5 shows that under the condition of the activated carbon mesh number of 20, the reaction time was greater than 30min, the reaction time affected the COD removal efficiency gently and the pH was the main factor influencing the COD removal efficiency. With the increase of pH, COD removal efficiency first increased and then decreased, and the COD removal efficiency reached the maximum when pH was 5.

3.2.2 Fitting optimization of activated carbon mesh number with the reaction time and pH

As shown in Fig.6 and Fig.7, through optimization analysis of various parameters, the reaction condition after optimization was as follows: the mesh number of activated carbons was 22, the pH was 5 and the reaction time was about 28 min.

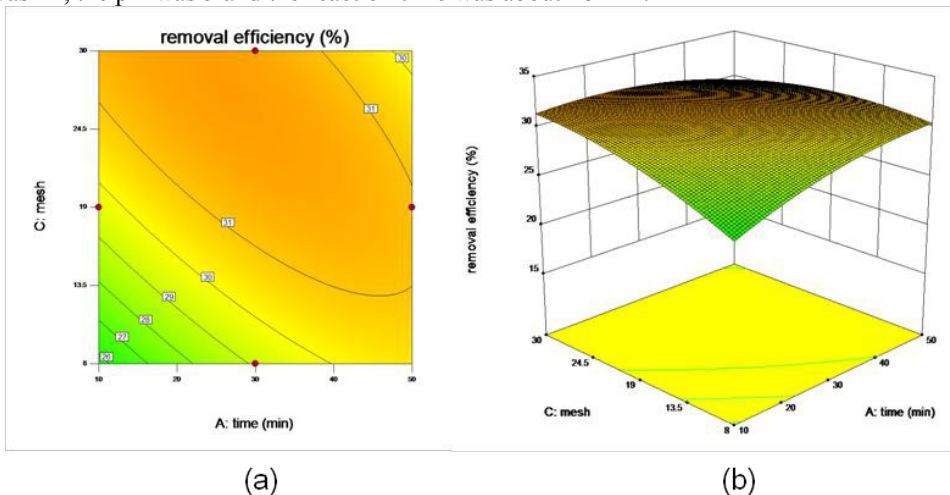


Fig. 6 Effect of reaction time and activated carbon mesh number on COD removal efficiency (a) contour map (b) response surface map

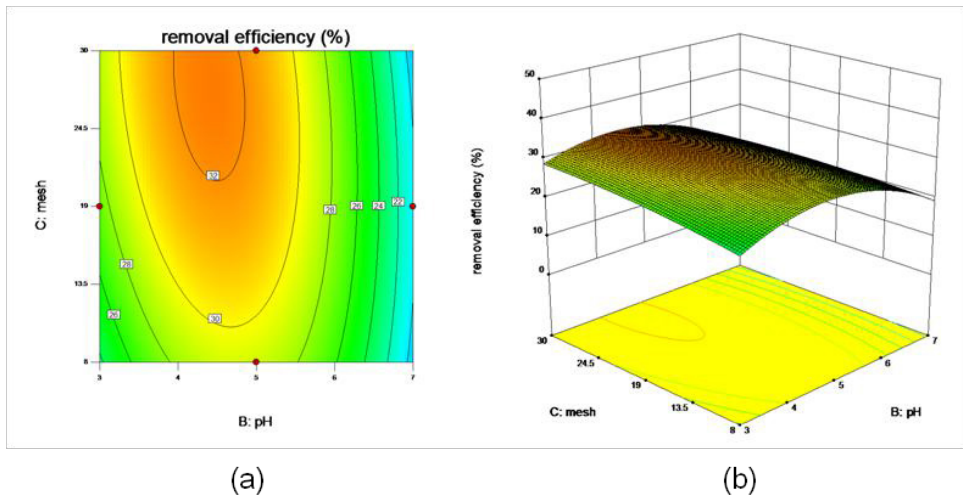


Fig. 7 Effect of pH and activated carbon mesh number on COD removal efficiency (a) contour map (b) response surface map

4 Conclusions

(1) The application of Ferro-carbon micro-electrolysis in the pretreatment of 1, 4-butanediol wastewater, can reduce the pollution load of subsequent systems and improve the biochemical property of wastewater.

(2) When the activated carbon mesh number was 20, pH value was 5 and reaction time was 30min, the removal efficiency of COD was 36.2%.

(3) RSM method was used to optimize the experimental results. The optimal working condition: activated carbon mesh number was 22, and pH value was 5 and reaction time was 28 min.

Through the analysis of experimental results by RSM, the relationship between each influencing factor and COD removal efficiency is conducted, as follows:

$$RI=30.6+0.077A-1.91B+0.19C+0.04AB+0.02AC+0.08BC$$

The reaction time and the mesh number of activated carbons have a positive effect on the COD removal efficiency, while the pH has a negative effect on the COD removal efficiency. The order of influence degree is: pH > the mesh number of activated carbons > reaction time, and pH has the greatest influence on the treatment rate of 1,4 butanediol wastewater by Ferro-carbon micro-electrolysis.

5 References

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