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Study on ferrite-attapulgite composite material as catalyst and adsorbent for chemical wastewater treatment

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ABSTRACT

The ferrite-attapulgite (ATP) composite with excellent catalytic activity was prepared and investigated to remove chemical oxygen demand (COD) from chemical wastewater. Effects of various factors, including catalyst preparation conditions, the dosage of H_2O_2, pH value, reaction time, and reaction temperature, were researched thoroughly. The orthogonal experiments on degradation process showed that the maximum removal rate of COD could be reached up to 91.3% under the optimal conditions ($pH = 5$, $H_2O_2 = 3.5\,mL$, $time = 120\,min$). The ferrite-ATP composite treated wastewater effectively and the chromaticity was reduced to 20 below when ferrous ion content occupied 5% of ATP and preparation temperature of the ferrite-ATP composite was 80℃, the effluent could be discharged after advanced treatment.

Keywords: Attapulgite; Catalytic oxidation; Chemical wastewater; Chemical oxygen demand

1. Introduction

Nowadays, the pollution from chemical wastewater is becoming a major environment problem due to the growing use of a variety of organics. Chemical sewage typically possess high chemical oxygen demand (COD), large amount of suspended solids, broadly fluctuating pH, and strong color caused by varying contaminates within water environment [1]. As recently reported, the high COD of wastewater breaks the chemical balances of water and brings a chief threat to human health [2]. Hence, it is necessary for underscoring the urgent need and raising awareness for efficient technology and materials to solve this environmental issue.

During recent years, several methods including chemical oxidation [3], reverse osmosis [4], biological treatment [5], membrane separation [6,7], adsorption [8,9], electrolytic process [10], etc. have been developed for treating industry wastewater. Among these methods, chemical oxidation is known as a common preprocessing method. Although, there are many advantages when chemical oxidation was applied individually, it also has some constraints which may cause inadequate effectiveness [11], which may due to the excellent oxidation effectiveness, no zwitterion manufactured in reactions, and weakly secondary pollution. The defects of oxidation reagent are that the high consumption of Fenton leads the increase of treatment costs to wastewater under high influent loads. On the other hand, it is easy to be carbonized when the ration of Fenton reagent is insufficient. Therefore, it is necessary to search cheap

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and efficient catalysts for the treatment of industrial wastewater [12].

Attapulgite (ATP) $[(Mg,Al)_4(Si)_8(O,OH,H_2O)_{26} \times nH_2O]$ is a hydrated magnesium aluminum silicate presenting in nature as fibrillate mineral [13,14]. It may also be defined as crystalline material, wherein the atoms in layers are cross-linked by chemical bones, while the atoms of adjacent layers interact by physical forces [15–17]. As reported, ATP performs unusual absorption properties and shows potential applications as nanocomposites [18,19], catalyst supports [20], and sustainable absorbents [21,22]. ATP materials have great advantages of low-cost, simple preparation, excellent absorbency, and regeneration. In this work, combining the excellent oxidation activity of ferrite and the good adsorption activity of ATP, ferrite-ATP composite material was investigated as catalyst in the treatment of chemical wastewater by chemical oxidation. The characterization of ferrite-ATP is that Fe^{2+} and H_2O_2 generates ·HO which can be absorbed in layers of ATP.

2. Experimental section

2.1. Materials

The sample of ATP used in the experiment was received from Jiangsu of China. The other chemicals were purchased in analytical purity and used without any purification. All solutions were prepared with distilled water.

2.2. Preparation of ferrite-ATP catalyst

2.2.1. Acid activation of ATP

Two hundred grams of ATP was acidified by HCl ($0.5\,mol\,L^{-1}$). The suspension was stirred for 5 h and kept standing at room temperature for 24 h. The mixture was filtered and washed several times with distilled water until pH~7. The sample was dried in a vacuum at 50℃ and then grounded.

2.2.2. Preparation of ferrite-ATP composite catalyst

The composite catalyst was prepared as following. The acid-activated ATP was dispersed into distilled water (at a mass ratio of 1:9) using ultra-sonification for 0.5 h, and then was added to 10% $FeSO_4$ solution (at different ratios) reacted for 1 h at different temperatures. The mixture was dried in an air oven at 105℃ and then transferred to beaker and kept aging for 24 h. The resulting sample was dried at 50℃ in order to eliminate the free water (i.e. adsorption water on the mineral surface by physical effect) and grounded to prepare ferrite-ATP composite catalyst.

2.3. Degradation experiment of chemical wastewater

Composite catalyst (0.5 g) and chemical wastewater (100 mL) were mixed in a 500 mL beaker, 3.0 mL H_2O_2 was added at a definite temperature. The pH value of the mixture system was adjusted with NaOH solution. After being stirred for 5 min, reaction was sustained for 2 h in infrared light. Ultimately, COD of chemical wastewater was determined.

COD of wastewater was determined according the potassium dichromate method of National Standard (China GB11914-89).

3. Results and discussion

3.1. Influence of catalyst preparation conditions on chemical wastewater treatment

3.1.1. Comparison between ATP and ferrite-ATP

Data of the raw wastewater and the treated wastewater are shown in Table 1. Zero point five grams of ferrite-ATP composite catalyst (6%) and 100 mL of chemical wastewater were mixed for 1 h at 70℃. As seen in Table 1, three data of different system were measured to research the effects of ferrite-ATP. The absorbing efficiency of ATP and ferrite-ATP in chemical wastewater is 17.12 and 82.52%, respectively. Wastewater treatment of ATP is based on physical adsorption,

Table 1
Comparison of chemical wastewater before and after treatment of ATP and ferrite-ATP catalyst

	Data of raw wastewater*			Data of treated wastewater			
	COD ($mg\,L^{-1}$)	NH_3-N ($mg\,L^{-1}$)	Chromaticity	Adsorbents	COD ($mg\,L^{-1}$)	NH_3-N ($mg\,L^{-1}$)	Chromaticity
Industrial wastewater	1,250	6.3	125	ATP	1,036	–	80
				Ferrite-ATP	218.5	1.86	24

*Chemical wastewater was obtained from a chemical plant in Lanzhou, pH < 2, salmon pink.

small molecule substances enter ATP channels early, and a small amount of organic materials enter later. Therefore, when adsorption is saturated, contaminants are almost no longer adsorbed in the channels of ATP. As shown in Table 1, it is obvious that the volume of COD influenced by ferrite-ATP was much larger than that by ATP. And the reason of the different treatment efficiency of ATP and ferrite-ATP is that wastewater treatment of ferrite-ATP is mainly based on chemical oxidation. It is in this way that Fe^{2+} and H_2O generated ·HO, macromolecular substances were oxidized to small molecule substances or biological materials which can be degraded.

3.1.2. *Effect of the ratio of Fe^{2+} and ATP*

As Figs. 1 and 2 show, it is obvious that residual COD and chromaticity drop gradually with the increase of Fe^{2+} content which transformed H_2O_2 to strong oxidant ·HO. The chromophore groups of organics in wastewater were oxidized to form small molecule substances. Meanwhile, ·OH which were produced by decomposition of H_2O_2 took part in the reaction completely. However, considering the actual engineering cost, the treatment of wastewater was effective and the chromaticity was reduced to 20 below when ferrous ion content occupied 5% of ATP.

3.1.3. *Effect of preparation temperature of ferrite-ATP catalyst*

When the preparation temperature reached 80℃, processing effect was better than others (Fig. 3). Probably, the reason was that magnesium oxide, silicon oxide, aluminum oxide, etc. which contained in ATP facilitated the ability of catalytic oxidation of ferrite. Excessive temperature urged ferrous ion to form FeOOH in ATP composite material. During the drying process, Fe_2O_3 was generated partially from FeOOH to $Fe(OH)_3$ by consuming the quality of ferrous ion. It causes the reduction of ·OH which come from the catalytic reaction of H_2O_2. On the other hand, lower temperature also reduced the activity of catalyst and reaction rate, which decreased the oxidation capacity of organic and the removal rate of COD. As shown in Fig. 3, the removal rate of COD decreased with the depression of reaction temperature when lower than 80℃.

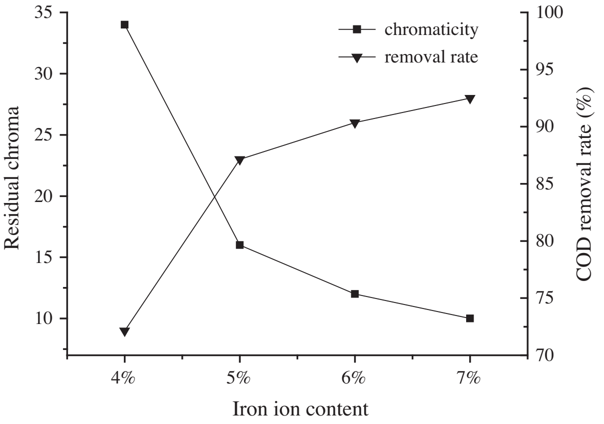

Fig. 2. Effects of iron ion content on chromaticity removal rate.

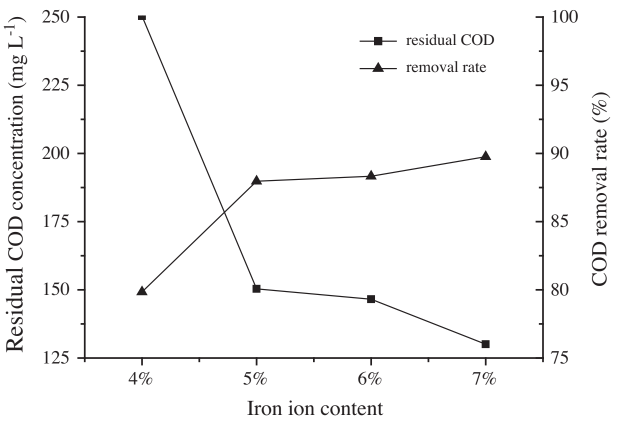

Fig. 1. Effects of iron ion content on COD removal rate.

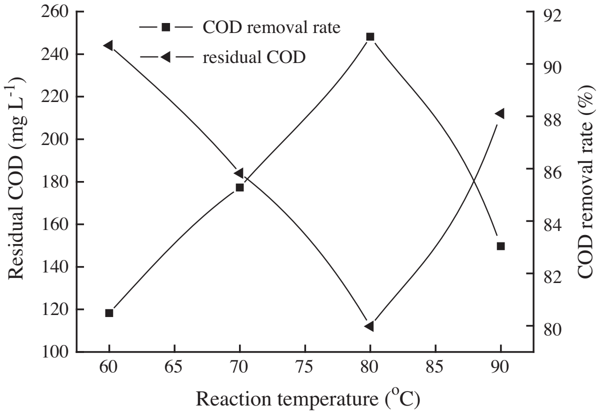

Fig. 3. Effects of temperature of preparation on COD removal rate. Volume of wastewater: 100 mL; pH of wastewater: 5; reaction time: 2 h.

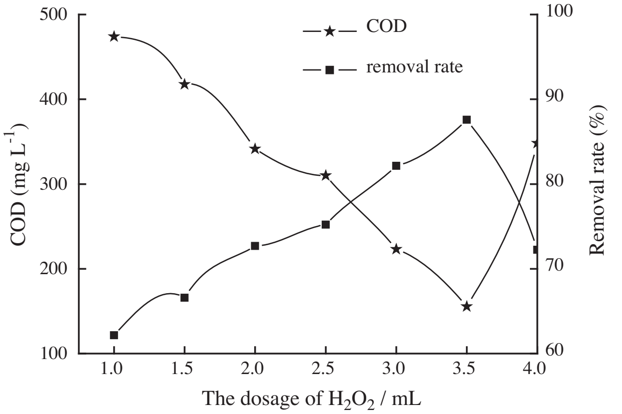

Fig. 4. Effects of quantity of H_2O_2 on COD removal rate. Volume of wastewater: 100 mL; pH of wastewater: 5; reaction temperature: 80℃.

3.2. Effect of various factors on treatment of chemical wastewater

3.2.1. Effect of the dosage of H_2O_2 on COD removal rate

Fig. 4 shows that the dosage of H_2O_2 has a direct effect on the removal rate of COD. Under low consumption of H_2O_2, the quantity and rate of ·HO decreased and treatment efficiency was constrained. With the high consumption of H_2O_2, ·HO which generated in the reaction was decreased. Originally, the content of ·HO in the reaction was consumed quickly. With time prolonging, the participation of ·HO was decreased gradually, all of which made reaction incomplete and wastewater presenting dark brown. Fractionated dosing hydrogen peroxide method [22] could be used to supplement ·HO. The effect was obvious, but the treatment cost is high. This study demonstrates that the removal rate of COD reaches the highest level, when the usage of H_2O_2 is 3.5 mL.

3.2.2. Effect of pH value

As reported, most pollutants in chemical wastewater are weak organic or bases, and different pH value of wastewater has different influence on the composition of pollutants which existed in wastewater [23]. Fig. 5 explains the effect of pH value on COD removal for investigation in this work. The removal rate of COD was obtained nearly 89% when the PH value was near 5.5 which was also the lowest COD value, as shown in Fig. 5. In acid condition, when the pH value was too low, the conversion from Fe^{2+} to Fe^{3+} occurred and the quantity of ·OH decreased, which affected the oxidation ability of ferrite-ATP for treatment. The relationship between pH value and COD removal is attributed to the number of active ·HO and Fe^{2+} which played a major role on the catalytic reaction. On the other hand, in the alkaline condition, the conversion from H_2O_2 to ·HO was inhibited, and Fe^{2+} lost the catalytic ability in the form of H_2O_2. Both cases resulted in the reduction of the quantity of Fe^{2+} in the samples.

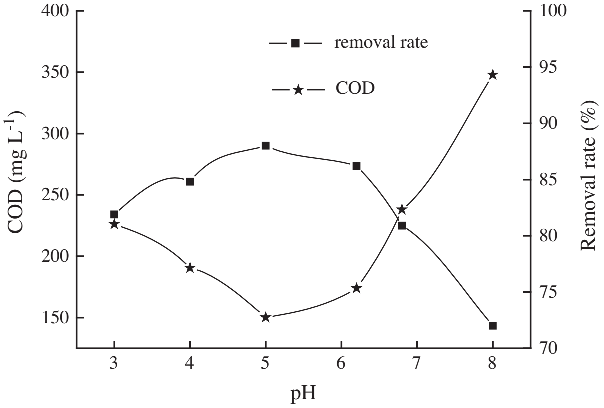

Fig. 5. Effects of pH on COD removal rate. Volume of wastewater: 100 mL; reaction time: 2 h; reaction temperature: 80℃.

3.2.3. Effect of reaction time

The effect of the reaction time on the catalytic capacities of ferrite-ATP was shown in Fig. 6. The removal rate of COD increased rapidly with the increasing of the reaction time from 20 to 50 min. When the reaction time was longer than 60 min, COD removal changed slowly. This might due to that iron ion and hydrogen peroxide in wastewater were both

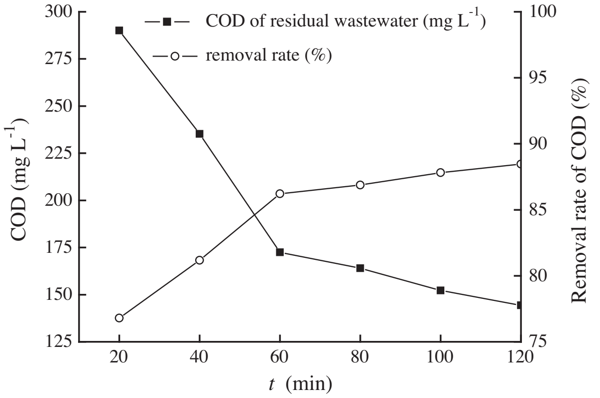

Fig. 6. Effects of reaction time on COD removal rate. Volume of wastewater: 100 mL; pH of wastewater: 5.5; reaction time: 2 h; reaction temperature: 80℃.

consumed and oxidation reduction potential decreased, which reduces the catalytic oxidation of the ferrite-ATP composite material.

3.2.4. Effect of reaction temperature

The effect of reaction temperature on COD removal under the optional conditions was investigated (Fig. 7). When the reaction temperature was increased from 20 to 50℃, the COD removal rate increased from 86 to 92℃. However, with further increasing temperature may enhance the activity of the ·OH and Fe^{2+}, but COD removal rate was drastic initially, the activity of ferrite-ATP and decomposition of H_2O_2 all reached equilibrium above 50℃. To be safe, an open container should be used in order to dispel the heat in the experimental process. In actual project, reaction below 50℃ can improve the activity and utilization ratio of catalyst.

3.3. Orthogonal experiments

The orthogonal experiments included three factors and three levels L9 (3^4). The pH, dosage of H_2O_2, and reaction time were used to determine the optimum condition of chemical wastewater treatment, and the interaction among factors was not considered (Table 2).

It is shown in Table 3 that the treatment efficiency of number 5 is the best and the removal rate of COD is up to 91.3%. And it is obvious that the dosage of H_2O_2 has greatest influence on treatment efficiency, pH takes the second place, and reaction time has the least influence. Hence, the optimum condition is A2B2C3, namely, pH = 5, H_2O_2 = 3.5 mL, and time = 120 min.

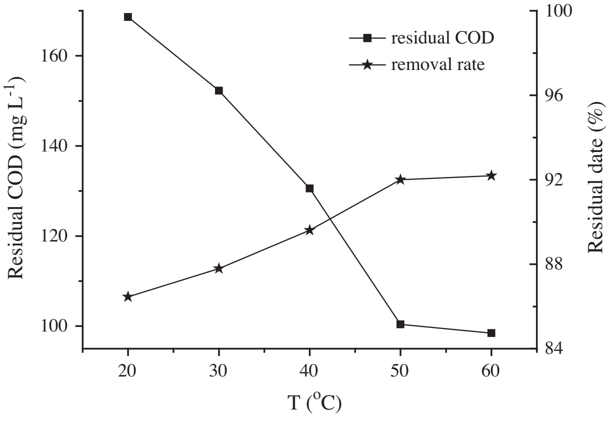

Fig. 7. Effects of temperature of wastewater on catalyst.

Table 2
Table of factors and levels

	A	B	C
Factors and levels	pH	The dosage of H_2O_2 (mL)	Reaction time (min)
Level 1	4	3	60
Level 2	5	3.5	80
Level 3	6	4	120

Table 3
Table of orthogonal experimental data analysis

Experiment number	A	B	C	Removal rate of COD（%）
1	A1	B1	C1	82.4
2	A1	B2	C2	87.1
3	A1	B3	C3	79.5
4	A2	B1	C2	84.3
5	A2	B2	C3	91.3
6	A2	B3	C1	81.2
7	A3	B1	C3	80.2
8	A3	B2	C1	82.5
9	A3	B3	C2	76.9
I	249.1	246.9	246.1	
Ⅱ	256.8	260.9	248.3	
Ⅲ	239.6	237.7	251	A2B2C3
R	17.2	23.2	4.9	

Table 4
Table of examine of orthogonal experimental data

Experiment number	COD (mg L^{-1})	Chromaticity	Removal rate of COD（%）
1	115	8.24	90.8
2	106	7.58	91.5
3	120	8.53	90.4

3.4. Validation of orthogonal experiments

According to the optimum condition of A2B2C3, Tests were repeated at pH = 5, H_2O_2 = 3.5 mL, and time = 120 min. The results show that the orthogonal experiment is credible (Table 4).

4. Conclusion

Ferrite-ATP composite material was prepared and used as catalyst in the treatment of chemical wastewater. The as-prepared ferrite-ATP composite shows excellent catalyst performance in treatment of chemical wastewater due to the excellent oxidation activity of ferrite with the good adsorption activity of ATP.

When the preparation condition of m (Fe^{2+})/m (ATP) was 5% and the preparation temperature of composite was 80℃, the composite material had excellent effect on chemical wastewater treatment. To research the influence on catalyst property in degradation process, the pH of wastewater, dosing quantity of H_2O_2, and reaction time were optimized through orthogonal experiments which showed that the optimum condition was A2B2C3. The greatest removal rate of COD was up to 91.3% when reaction time was 2 h in infrared light under the optimal conditions and then the effluent could be discharged after advanced treatment.

Nomenclature

ATP	—	attapulgite
COD	—	chemical oxygen demand

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