

## Study on Preparation and Characterization of Heterogeneous Fenton Catalyst

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### Abstract

Homogeneous Fenton method has the characteristics of fast reaction and good degradation effect, but its economic cost is relatively high. If  $\text{Fe}^{2+}$  is not treated, it will also cause pollution. In order to make up for this defect, heterogeneous catalyst is considered to be prepared to use heterogeneous system to degrade benzoic acid wastewater. In this paper, the purchased AC particles were first crushed, graded and pretreated. Taking the pretreated sample as the carrier, the Fe / AC catalyst was prepared by immersing the carrier in 1g / L  $\text{Fe}^{2+}$  solution. The influence factors of catalyst preparation were analyzed by orthogonal test. It was found that the influence of particle size, calcination temperature and calcination time on catalyst activity increased in turn. Combined with TG-DSC, BET, XRD, SEM and other testing methods to characterize the supported catalyst, the optimal preparation conditions were determined to be a particle size of 60-100 mesh and calcined at 300°C for 4 h.

### Keywords

Heterogeneous; Fenton; Catalyst.

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## 1. Introduction

The traditional homogeneous Fenton method is very effective for the treatment of aromatic organic compounds in wastewater, which has the characteristics of high efficiency and convenient operation. Many researches are related to the treatment of organic chemical wastewater. But in the actual application process, the traditional Fenton technology will produce iron sludge in the reaction process, which needs further follow-up treatment, which increases the economic cost of wastewater treatment. In order to solve the above problems, scholars put forward heterogeneous methods. At present, there are many reports about the preparation and application of heterogeneous Fenton catalyst [1-5]. However, due to the disadvantages of complex preparation method, poor catalytic effect and more iron dissolution, the preparation of new high-efficiency catalyst still needs further study. Based on the previous research, this experiment prepared a heterogeneous catalyst by impregnating the AC of the particles into a ferrous ion solution.

## 2. Experiment

### 2.1 Experimental reagent

Ferrous sulfate, 30% hydrogen peroxide, sodium hydroxide, hydrochloric acid and sulfuric acid are all analytically pure and purchased in Tianjin Jiangtian Chemical Technology Co., Ltd. Coconut shell

granular activated carbon (AC) was purchased from Chengde Yibei Yanshan Activated Carbon Co., Ltd.

## 2.2 Preparation of catalyst

Activated carbon pretreatment: A certain amount of activated carbon was weighed in a 250ml beaker, and 10% HCl solution was added to the beaker to make the activated carbon fully immersed. The activated carbon was washed in an ultrasonic cleaner for 40min, washed with distilled water, and then put into an oven set at 105°C to dry and prepare.

The catalyst was prepared by impregnation. A certain amount of pretreated activated carbon is immersed in FeSO<sub>4</sub> solution with Fe<sup>2+</sup> concentration of 1000mg / L. Under room temperature, it is evenly stirred on the magnetic stirrer for 12h, then it is allowed to stand for 12h. After filtration, it is put in the oven and dried at 105°C for 12h. It is calcined at a certain temperature in nitrogen atmosphere for a period of time, washed and dried, and the obtained catalyst is marked.

## 2.3 Experimental method

500mL of simulated benzoic acid wastewater was added to the reactor, which was stirred on a constant temperature magnetic agitator. A certain amount of catalyst was added and stirred overnight. After reaching adsorption saturation, dilute H<sub>2</sub>SO<sub>4</sub> or NaOH solution was used to adjust the solution to the desired pH value, and a certain amount of 30% H<sub>2</sub>O<sub>2</sub> was added to start the reaction. The samples were taken at the specified interval, and the filter membrane was immediately pumped with 0.22m. The filtrate pH was about 10 to stop the reaction, and the liquid to be measured was taken for TOC index analysis.

## 2.4 Analysis method

TOC value was determined by total organic carbon (TOC) analyzer in Ge sieversinnovx laboratory. The pH value was determined by Hanna instruments ph211 precision acidimeter. TG-DSC test was carried out with labsysevo sta of Setaram company in France. The heating rate was 10°C•min<sup>-1</sup>, the final reaction temperature was 800°C, the carrier gas was high purity nitrogen, and the gas flow rate was 40 ml / min. The adsorption / desorption isotherms of nitrogen at 77.35k were determined by using Canta autosorb IQ automatic specific surface and pore size distribution analyzer. The specific surface area of the sample was calculated by the BET equation and by the relative pressure p / p. The total pore volume was calculated by the nitrogen adsorption amount around 0.99, and the pore size distribution was analyzed by the DFT method. MSAL XD-3 diffractometer was used to analyze the crystal phase of the samples. The test conditions were: tube voltage was 36kV, tube current was 20 mA, Cu K $\alpha$ , and the scanning range was 10 °-70 °. The appearance characteristics of AC and Fe / AC catalysts were observed by Hitachi scanning electron microscope su1510.

# 3. Results and discussion

## 3.1 Orthogonal experiment

(1) Factor level of orthogonal test

Table 1

Factor level	A Particle size(mesh)	B Calcination time (h)	C calcination temperature (°C)
1	20-30	2	200
2	30-60	3	300
3	60-100	4	400

(2)  $L_9(3^4)$  Orthogonal experiment

Table 2

Factor Labor-atory number	A Particle size(mesh)	B Calcination time (h)	C calcination temperature (°C)	TOC(ppm) raw water (51.2)	TOC removal rate (%)
1	20-30	2	200	39.15	23.54
2	20-30	3	300	35.4	30.86
3	20-30	4	400	35.7	30.27
4	30-60	2	300	23.4	54.3
5	30-60	3	400	26.9	47.46
6	30-60	4	200	23.6	53.91
7	60-100	2	400	17.5	65.82
8	60-100	3	200	19.7	61.52
9	60-100	4	300	17.1	66.6

## (3) Analysis of experimental results

Table 3

Factor Calcu-lated value	A Particle size(mesh)	B Calcination time (h)	C calcination temperature (°C)
$K_1$	84.67	143.66	138.97
$K_2$	155.67	139.84	151.76
$K_3$	193.94	150.78	143.55
$k_1$	28.22	47.89	46.32
$k_2$	51.89	46.61	50.59
$k_3$	64.65	50.26	47.85
R	36.43	3.65	4.27

## (4) Result analysis

Direct comparison with table 2 shows that among the nine experimental results, the TOC degradation rate of the catalyst prepared in Experiment 9 is the best, with the level combination of 60-100 mesh, calcination for 4h, and 300 °C, which are the most influential levels among all factors. In addition, it can be seen that the optimal combination of factors in this experiment is A3, B3, C2, and through the size of R value, it can be seen that there is a significant sequence of factors in this experiment, the primary and secondary relationship is particle size > calcination temperature > calcination time, that is to say, the main factor affecting the removal rate of TOC is particle size, followed by calcination

temperature and calcination time. The preparation conditions of the catalyst were determined to be 60-100 mesh, calcined for 4 hours and calcined at 300°C .

#### 4. Conclusion

Through the orthogonal design, the factors that affect the preparation of catalyst were analyzed. It was found that these three factors have obvious influence on the performance of catalyst, the biggest one is the particle size, the second one is the temperature when calcining in muffle furnace, and the least one is the calcination time. Through the analysis of the above data, the preparation condition was determined to calcine 60-100 mesh particles at 300°C for 4 hours.

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