Experimental Research on Treatment of Methylene Blue Wastewater by Fe3O4-MnO2 Fenton System

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Abstract In order to broaden the processing conditions of the Fenton method, under the premise of adding a catalyst, the operating conditions of the Fenton-like system were studied. When studying Fe3O4-MnO2-PAC composite material as a catalyst, this experiment find the influence of different single factors on the Fenton-like system. Research shows that when the pH is 2-5, the dosage of Fe3O4-MnO2-PAC is 800mg/L, the dosage of H2O2 is 0.8mol/L, the reaction temperature is 10℃-50℃, Fe3O4-MnO2-PAC catalyst. When used less than five times, it has a better degradation effect on methylene blue wastewater.

1. Instruction
Due to the improvement of people's living standards and the rapid development of the dye industry, the composition of printing and dyeing wastewater has become more and more complex and the amount of drainage increased. Printing and dyeing wastewater has become one of the important factors affecting my country's water environment.1-3 Printing and dyeing wastewater has the characteristics of large changes in water quality and quantity, high COD content, high chroma, high toxicity and poor biodegradability.4-7 Fenton oxidation method has many advantages, but this method also has many shortcomings, such as large dosage of chemicals, narrow application range of pH value, low utilization rate of H2O2 and catalyst, high treatment cost, and iron sludge in the effluent 8-9. In this paper, the Fe3O4-MnO2 composite material was prepared by the chemical co-precipitation method and loaded on the powder activated carbon with relatively large void structure. Then the Fe3O4-MnO2-PAC composite material was used as a catalyst to study the degradation effect of Fe3O4-MnO2-PAC-based Fenton system on methylene blue wastewater. By controlling the single factor, the optimal reaction conditions were explored, and the degradation effect under the optimal conditions was studied.

2. Results and analysis
2.1 Influence of initial pH value on treatment effect
Take 12 test water samples, each 100 mL, and add them to 12 500 mL beakers. The chromaticity is 1533.5 (times), and the COD concentration is 166.5 mg/L. The pH value was adjusted by dilute sulfuric acid or sodium hydroxide, and the test water sample was continuously mechanically stirred for
3 hours with a six-joint mixer. The effect of pH value on the degradation test wastewater treatment effect of the Fenton-like system was studied. The result is shown in Figure 1.

![Figure 1. The influence of PH](image)

The reason for the above phenomenon is that under acidic conditions, a large amount of hydrogen ions will quickly capture the ·OH in the reaction and react to form H2O. The reduction of ·OH in the solution makes the treatment effect poor. As the pH increases, the H+ concentration decreases and the removal rate slowly increases. When the pH is 3-5, the removal rate shows a downward trend but the downward trend is slow, which is caused by the weakening of the catalytic degradation ability of the Fe3O4-MnO2-PAC catalyst. Compared with the conventional Fenton method, the optimum pH range of this type of Fenton method is expanded to 2-5, which improves the experimental conditions.

2.2. The effect of Fe3O4-MnO2-PAC catalyst dosage on treatment effect

Take 9 water samples of methylene blue, each 100mL, each water sample has a color of 1522.7 (times) and a COD concentration of 165.8mg/L, and add them to 9 500mL beakers. Adjust the pH to 3 with the prepared dilute sulfuric acid solution, first add the amount of H2O2 to 0.8Qth, and then add the catalyst Fe3O4-MnO2-PAC to each beaker in turn, and place it in the six-joint mixer for continuous mechanical stirring for 3 hours. The result is shown in Figure 2 below.
Figure 2. The influence of Fe3O4-MnO2-PAC catalyst dosage

It can be seen from Figure 2 that when the amount of catalyst Fe3O4-MnO2-PAC is in the range of 0.1g/L-0.8g/L, the amount of catalyst added is directly proportional to the chroma and COD removal rate. When the catalyst Fe3O4-MnO2-PAC is added 0.8g/L, the removal rate reaches the highest. When the dosage of Fe3O4-MnO2-PAC catalyst is in the range of 0.8g/L-2.0g/L, the chromaticity removal rate of methylene blue has been maintained above 98%, but the removal efficiency of COD is proportional to the dosage of catalyst inversely. Therefore, the optimal dosage of Fe3O4-MnO2-PAC in this type of Fenton system is 0.8g/L.

2.3. The influence of H2O2 dosage on the treatment effect

Take 9 test water samples, add 100ml each into 9 500ml beakers, the chromaticity is 1523.5 (times), and the COD concentration is 166mg/L. Adjust the pH to 3 with the prepared dilute sulfuric acid solution, first add the catalyst Fe3O4-MnO2-PAC to 0.8g/L, and then add H2O2 to each beaker in turn, and put it into the six-joint mixer. Stir for 180min. The effect of the dosage of H2O2 on the test is shown in Figure 3 below.
Figure 3. The influence of H2O2 dosage

It can be seen from the above figure that the dosage of H2O2 has a significant effect on the treatment effect. In the range of $0.1Q_{th}$-$0.8Q_{th}$, the dosage of H2O2 is proportional to the chromaticity removal rate in the wastewater, and the chromaticity removal rate increased from the initial 46.85% to 98.93%. When the dosage of H2O2 is greater than $0.8Q_{th}$, H2O2 has little effect on the chroma removal rate. When the dosage of H2O2 is less than $0.8Q_{th}$, the removal efficiency of COD increases with the increase of the dosage of H2O2 from the initial 15.96% to 80.36%. The removal rate reaches its peak at $0.8Q_{th}$, and the effluent COD concentration is 32.6mg/L. After that, if H2O2 is added, the removal rate will drop sharply.

After comparing with the conventional Fenton method, it is found that the Fe3O4-MnO2-PAC-based Fenton system saves the dosage of H2O2, and the removal effect is also higher than that of the conventional Fenton method. Therefore, the dosage of H2O2 is finally determined for $0.8Q_{th}$.

2.4. Study on the service life of Fe3O4-MnO2-PAC catalyst

After the above tests, the optimal test conditions for the test research are determined as: The influent color is 1522.6 (times), the influent COD is about 165.3mg/L wastewater, the pH is adjusted to 3, the dosage of the catalyst Fe3O4-MnO2-PAC is 0.8g/L, and the dosage of H2O2 is $0.8Q_{th}$, fully react for 120min at a temperature of 25°C. After the reaction, the Fe3O4-MnO2-PAC catalyst was effectively recovered with a magnet. The catalyst was repeatedly washed with distilled water several times and then used in the next test. The test was repeated ten times to investigate the effect of the catalyst on methylene blue and COD after repeated use. The effect of removal rate is shown in Figure 4 below.
Figure 4. The influence of the number of catalyst reuses

It can be seen from Figure 4 that when the number of uses of the catalyst is less than five times, the number of uses of the catalyst has little effect on the color removal rate of the test wastewater. The COD content of the effluent from the five reactions was 24.06mg/L, 25.84mg/L, 28.84mg/L, 32.71mg/L, 37.19mg/L, respectively. When the catalyst is used less than five times, the COD content in the effluent quality meets the national standard. When the catalyst is used more than five times, the chroma removal rate begins to decrease, and the removal rate decreases from 96.35% to 82.26%. The decreasing trend of COD removal efficiency is also more obvious, the removal rate is reduced from 72.67% to 47.42%. When the catalyst is used more than ten times, the COD content of the effluent is 87.49mg/L, and the effluent quality has not reached the discharge standard.

3. Results and discussion

(1) Too much or too little dosage of medicament has an inhibitory effect on the entire reaction. Finally, we determined that the dosage of H2O2 was 0.8Qth, and the dosage of catalyst Fe3O4-MnO2-PAC was 0.8g/L.

(2) The study of Fenton-like system to treat methylene blue wastewater broadens the effective range of pH, so that the reaction has a better degradation effect between pH=2-5, and to some extent, it improves the shortcomings of the conventional Fenton oxidation method with a narrow range of available pH.

(3) Fe3O4-MnO2-PAC composite material is a reusable material, after the Fe3O4-MnO2-PAC catalyst was reused five times, the color removal rate of methylene blue was still close to 100%, and the removal efficiency of COD was 77.65%.

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