Experimental study on treatment of malachite green wastewater by single iron heterogeneous fenton system

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Abstract: The effect and influencing factors of single-iron heterogeneous Fenton system in the treatment of malachite green wastewater were experimentally studied. The test results show that: the initial pH is 3, the dosage of Fe/AC heterogeneous catalyst is 2g/L and after the reaction is 120min, the wastewater color removal rate can reach 92.01%, and COD removal rate can reach 78.95%.

1. Introduction

The printing and dyeing industry will produce a large amount of sewage and waste water. Fenton reagent method is one of the most effective methods to treat difficult-to-degrade printing and dyeing wastewater [1]. However, the traditional Fenton reagent method has a narrow pH range, low H2O2 utilization rate, a large amount of catalyst and non-renewable, thus improving the Fenton reagent method treatment process cost [2]. Using the heterogeneous Fenton method to treat the difficult-to-degrade printing and dyeing wastewater can effectively avoid the problems of the traditional Fenton reagent method, such as the narrow pH range of the reaction, the easy formation of iron sludge and secondary pollution, and the inability to recycle the chemicals[3]. Ramirez et al.[4] used activated carbon as the carrier and single iron ion as the active component to prepare Fe/AC heterogeneous catalyst and H2O2 to form a heterogeneous Fenton system to treat orange-II dye wastewater. The results showed that after 4 hours of degradation reaction, the removal rate of orange-II dye was as high as 90%. By supporting single iron ions on the catalyst carrier, a heterogeneous catalyst is formed. This kind of catalyst can overcome the shortcomings of narrow reaction pH range, large dosage of medicament and unable to be recycled, effectively improve the catalytic performance of the catalyst, and effectively treat malachite green wastewater.

2. Materials and Methods

2.1. Experimental equipment

2.1.1. System experiment device

The test device for the heterogeneous Fenton system test uses a six-unit mixer. The schematic diagram of the device is shown in figure 1, and the physical diagram of the device is shown in figure 2.
2.1.2. Test equipment
Ultraviolet germicidal lamp, ultraviolet-visible spectrophotometer, lightning pH meter, electrothermal constant temperature blast drying oven, muffle furnace, electronic analytical balance, glassware, six-unit electric mixer, magnetic stirrer, motor stirrer, digital display thermostat water bath.

2.1.3. Test reagent
Malachite green dye, powder activated carbon, 30% hydrogen peroxide, sodium bicarbonate, potassium dichromate, sulfuric acid, potassium hydrogen phthalate, hydrochloric acid, potassium aluminum sulfate, ammonium molybdate, mercury sulfate, ferrous sulfate heptahydrate, silver sulfate.

Preparation of Fe/AC heterogeneous catalyst: The Fe/AC heterogeneous catalyst was prepared by impregnation method. A scanning electron microscope (SEM) was used to photograph the heterogeneous catalyst to observe the macroscopic appearance and structure characteristics of each material. The scanning result of the electron microscope is shown in figure 3.

2.1.4. Test water sample
The wastewater used in this experiment is a self-prepared water sample to simulate printing and dyeing wastewater, and the main component is malachite green dye. The color of the water sample is 300-350, and the initial COD concentration is 350-400mg/L.

2.2. Test method and analysis method

2.2.1. Test method
The Fe/AC heterogeneous catalyst is prepared by impregnation method. The test prepares a certain concentration of malachite green solution in a 1000mL volumetric flask, takes a certain amount of malachite green solution into a 500mL beaker, adjusts the pH value at room temperature (25°C), and adds a certain amount of Fe²⁺, different loading concentrations of Fe/AC heterogeneous catalyst and 30% H₂O₂. The optimal preparation conditions of Fe/AC were determined by investigating the wastewater chromaticity and COD removal effect.

2.2.2. Analysis method
The chromaticity is measured by the dilution factor method. The COD is determined by rapid airtight
catalytic digestion method. The pH value is determined by a magnetic pH meter.

3. Results & Discussion

3.1. Research on the factors affecting the treatment of malachite green wastewater by the single-iron heterogeneous Fenton system

3.1.1. The effect of initial pH on the treatment effect
The test uses 8 500mL beakers, each measuring 100mL malachite green wastewater with a colority of 324.5 times and a COD mass concentration of 351mg/L. The test adjust the pH of the wastewater to 1, 2, 3, 4, 5, 6, 7, 8 with dilute sulfuric acid and sodium bicarbonate, and then add 2g/L of Fe/AC heterogeneous catalyst and Qth=2.4ml /L 30%H2O2. Use a six-joint mixer to continue mechanical stirring for 120 minutes. After the reaction is over, the supernatant is taken to measure the color removal rate and COD removal rate. The test results are shown in figure 4.

![Figure 4 Effect of pH on treatment effect](image)

It can be seen from figure 4 that the initial pH value of malachite green wastewater still has a large impact on the chroma and COD removal rate. When the pH is 3, the removal rate of chroma and COD is as high as 91.07% and 74.76%. When the pH value is 8, the chroma and COD removal rate are the lowest, which are 73.92% and 36.24%, respectively. When the pH value is too high, the active components Fe²⁺ and Fe³⁺ in the catalyst are prone to produce hydroxide precipitation or other complexes, thereby affecting the catalytic ability of the catalyst and further affecting the wastewater treatment effect. In summary, the optimal pH value of this reaction is 3.

3.1.2. The influence of the dosage of Fe/AC heterogeneous catalyst on the treatment effect
The test uses 8 500mL beakers, each measuring 100mL malachite green wastewater with a color degree of 322.1 times and a COD mass concentration of 348.5mg/L. The pH of the wastewater is adjusted to 3 with dilute sulfuric acid. Add 0.05g, 0.1g, 0.15g, 0.2g, 0.25g, 0.3g, 0.35g, 0.4g of Fe/AC heterogeneous catalyst respectively. Then add 30% H2O2, with Qth=2.4ml/L, and finally use a six-joint mixer to continue mechanical stirring for 120 minutes. After the reaction is over, take the supernatant to measure its color removal rate and COD removal rate. The test results are shown in figure 5.

![Figure 5 Influence of catalyst dosage on treatment effect](image)
It can be seen from figure 5 that with the continuous increase in the dosage of Fe/AC heterogeneous catalyst, the chromaticity removal rate first increased and then remained basically unchanged, and the COD removal rate first increased and then decreased the trend of. When the catalyst dosage is 0.2g, the chroma and COD removal rate both reach the highest, which are 90.76% and 76.35% respectively. In summary, the optimal catalyst dosage for this reaction is 0.2g.

3.2. Research on the treatment effect of malachite green wastewater under optimal reaction conditions

The best single factor determined by the above single factor experiments is pH 3, the dosage of Fe/AC heterogeneous catalyst is 2g/L, and the dosage of 30% H2O2 is 1.25Qth, which is 3ml/L. The time is 120min. Under the optimal reaction conditions, the malachite green wastewater is treated. The specific test steps: use a 500mL beaker to measure 300mL malachite green wastewater with a color of 324.0 times and a COD concentration of 351.0mg/L, and adjust the pH 3. The dosage of Fe/AC heterogeneous catalyst is 2g/L, and the dosage of 30% H2O2 is 1.25Qth, which is 3ml/L. At room temperature (25°C), use a six-joint mixer for continuous stirring for 120 minutes. Take the supernatant at 10min, 20min, 30min, 40min, 50min, 60min, 70min, 80min, 90min, 100min, 110min, 120min every 10min, and measure the chroma removal rate and COD removal rate. The test results are shown in the figure 6.

Figure 5 Effect of catalyst dosage on treatment efficiency

Figure 6 Effect of treatment under optimal reaction conditions
It can be seen from figure 6 that under the optimal reaction conditions, the chromaticity and COD removal effect of malachite green dye wastewater is very obvious. At 120 minutes, the chroma removal rate has reached 92.01%, and the effluent chroma is 25.89 times. At 120 minutes, the COD removal rate reached 78.95%, and the effluent COD concentration was 73.89mg/L. At this time, the chromaticity and COD concentration of the effluent after treatment met the limits of "Water Pollutant Discharge Standard for Textile Dyeing and Finishing Industry (GB4287-2012)". The value is specified and can be discharged directly.

4. Conclusions
(1) The single-iron heterogeneous Fenton system has a good treatment effect on malachite green simulated printing and dyeing wastewater. When the initial pH of the wastewater is 3, the dosage of Fe/AC catalyst loaded with 1mol/LFe2+ is 2g/L, and the reaction time is 120min. The system has the best treatment effect on malachite green wastewater. After treatment, the chromaticity removal rate of malachite green wastewater can reach 92.01%, the effluent chromaticity is 25.89 times, the COD removal rate reaches 78.95%, and the effluent COD concentration is 73.89mg/L.

(2) The initial pH value still has a great influence on the wastewater treatment effect. The Fe2+ loaded on the powder activated carbon carrier will continuously dissolve and lose from the surface of the carrier during the reaction, thereby reducing the utilization rate of the catalyst.

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