

# Preparation of magnetic nanomaterials and their adsorption properties for phenol in wastewater

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**Abstract:** In this study, magnetic Nano-FeO<sub>4</sub> particles were prepared and amino-modified with APTES. The materials were characterized by TEM, SEM and other techniques. Moreover, the adsorption of phenol in water by amino-modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles was investigated, and the effects of adsorbent dosage, adsorption time, pH value, temperature and initial concentration on adsorption removal rate were determined.

**Keywords:** amino modification, magnetic nanomaterials, phenol, adsorption

## 1. Introduction

With the rapid development of the petrochemical industry, environmental degradation has become increasingly severe. In particular, phenol-containing wastewater produced by the resin-manufacturing, pharmaceutical, and pesticide industries has led to severe environmental pollution. Due to the characteristics of benzene structure, such substances are difficult to degrade naturally in nature. Among the treatment technologies for phenol-containing wastewater, adsorption is a highly effective method. In this experiment, amino-modified magnetic nanomaterials were adopted to realize phenol adsorption as well as its rapid and efficient separation, which provides a theoretical basis for industrialized adsorption.[1]-[4]

## 2. Experimental section

### 2.1. Preparation of nano-Fe<sub>3</sub>O<sub>4</sub> particles

3-Aminopropyltriethoxysilane (APTES), Acetone (Sinopharm Group), Anhydrous Ethanol (Sinopharm Group), Glacial Acetic Acid (Sinopharm Group), Ferric Chloride (Sinopharm Group), Ethylene Glycol (Sinopharm Group), Polyethylene Glycol (Sinopharm Group), Sodium Acetate (Sinopharm Group), Deionized Water (University of Science and Technology of China), Transmission Electron Microscope (Hitachi H7650, accelerating voltage 100 kV), Scanning Electron Microscope (Hitachi X-650 field-emission scanning electron microscope, accelerating voltage 5.0 kV), Ultrasonic Cleaner, pH Meter, Hydrothermal Autoclave

### 2.2. Preparation of Nano-Fe<sub>3</sub>O<sub>4</sub> particles

Weigh 1.2 g ferric chloride and dissolve it in 25 mL ethylene glycol, then add 2.5 g sodium acetate and 1.0 g polyethylene glycol. Stir the mixture on a magnetic stirrer for 30 min, perform ultrasonic oscillation for 20 min, and transfer it into a hydrothermal autoclave. React in a constant-temperature oven at 190 °C for 6 h, followed by natural cooling to room temperature. Under the effect of an external magnetic field, wash the product repeatedly with deionized water and anhydrous ethanol alternately. Reaction principles:



### 2.3. Amino-modified Fe<sub>3</sub>O<sub>4</sub> particles

Fe<sub>3</sub>O<sub>4</sub> nanoparticles were activated by amino-modification [5] and other methods. Weigh 0.5 g of activated Fe<sub>3</sub>O<sub>4</sub> and disperse it into 100 mL solution composed of ethanol and water (1 mL). Ultrasonically disperse the solution for 20 min. Add 1 mL APTES dropwise at a rate of one drop every 10 min under low-speed stirring for 10 h. After the reaction, wash the product several times alternately with anhydrous ethanol and deionized water to obtain amino-modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

### 2.4. Adsorption experiment

In a 150 mL conical flask, add 50 mL phenol solution of a certain concentration and the modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Disperse the mixture by ultrasonic oscillation for a certain period of time, then perform separation. The adsorption removal rate is obtained by determining the residual phenol content (4-aminoantipyrine spectrophotometric method).

### 2.5. Reusability experiment

Under the optimal experimental conditions, the separated amino-modified Fe<sub>3</sub>O<sub>4</sub> nanomaterials were regenerated and used to adsorb fresh solution again. After repeated experiments, the decline of adsorption capacity was investigated.

## 3. Results and discussion

### 3.1. TEM analysis

It can be seen from Figure 1 that the particle size is larger than 50 nm, showing a slight increase compared with unmodified Fe<sub>3</sub>O<sub>4</sub>. Meanwhile, the TEM images reveal that the core morphology of particles is nearly spherical, and other morphologies appear on the surface. The increase in particle size and morphological changes may result from the following reasons: The coating layer of APTES leads to thickness increase; Thickness growth caused by possible cross-linking between APTES coated on particles; Agglomeration induced by the intrinsic magnetism of particles.

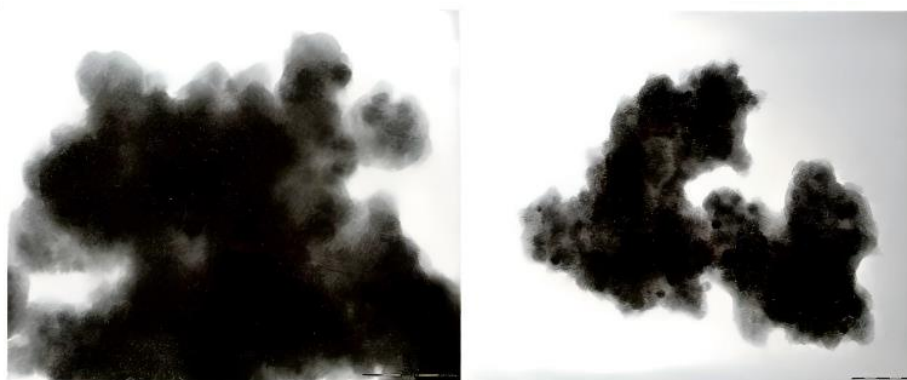


Figure 1 TEM characterization

### 3.2. SEM analysis

It can be observed from Figure 2 that the surface morphology of modified Fe<sub>3</sub>O<sub>4</sub> changes from spherical to cotton-like shape. Close observation of Figure 3 shows that these structures are still mainly composed of sphere-like units. Such morphological variation may be attributed to the agglomeration of Fe<sub>3</sub>O<sub>4</sub> nanoparticles triggered by amino groups after amino modification. Despite the occurrence of agglomeration, the dispersed cotton-like structure still improves the adsorption performance.

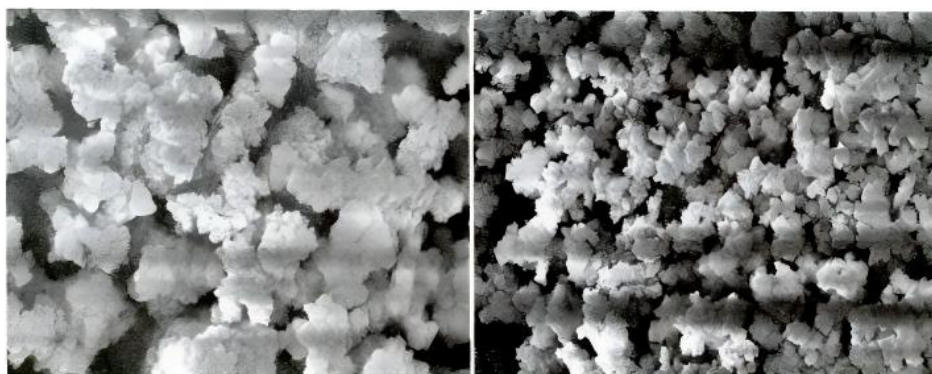


Figure 2 SEM characterization

### 3.3. Effect of adsorption time on removal rate

In a 150 mL conical flask, 50 mL phenol solution with a concentration of 50 mg/L and 0.3 g modified  $\text{Fe}_3\text{O}_4$  nanoparticles were added, and the results are shown in Figure 3. As can be seen from Figure 3, the phenol removal rate gradually rises with the increase of adsorption time, while the increasing rate gradually slows down. Little change occurs in the removal rate after the adsorption time reaches 15 min, indicating that the adsorption dynamic equilibrium is basically achieved. Prolonging the adsorption time cannot further improve the removal rate.

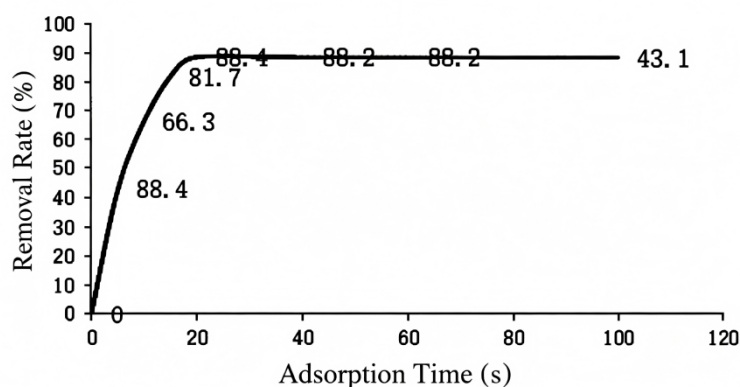


Figure 3 Effect of adsorption time on removal rate

### 3.4. Effect of pH on removal rate

In a 150 mL conical flask, 50 mL phenol solution at a concentration of 50 mg/L and 0.3 g modified  $\text{Fe}_3\text{O}_4$  nanoparticles were added, and the results are presented in Figure 4. It can be seen from Figure 4 that the phenol removal rate rises gradually with the increase of pH in the adsorption environment, and reaches 90.1 % at pH = 10. This is because phenol mainly exists in the form of anions in solution. When interacting with amino-modified  $\text{Fe}_3\text{O}_4$  particles, the cations adsorb phenol anions to a considerable extent. Considering the industrial cost, pH = 9 was selected in this experiment.

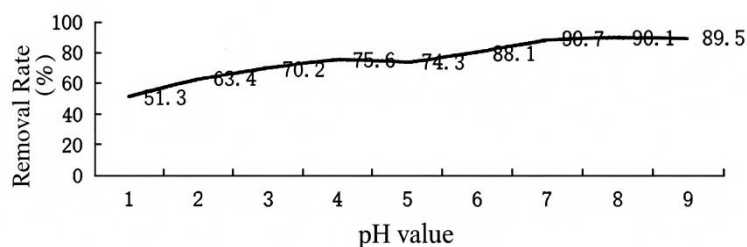


Figure 4 Effect of pH on adsorption removal rate

### 3.5. Effect of dosage on removal rate

In a 150 mL conical flask, 50 mL phenol solution with a concentration of 50 mg/L and modified  $\text{Fe}_3\text{O}_4$  nanoparticles were added, and the results are shown in Figure 5. As can be seen from Figure 5, the phenol removal rate increases gradually with the rising dosage of aminated  $\text{Fe}_3\text{O}_4$  nanoparticles, whereas the growth rate slows down. The removal rate hardly changes when the dosage exceeds 0.3 g.

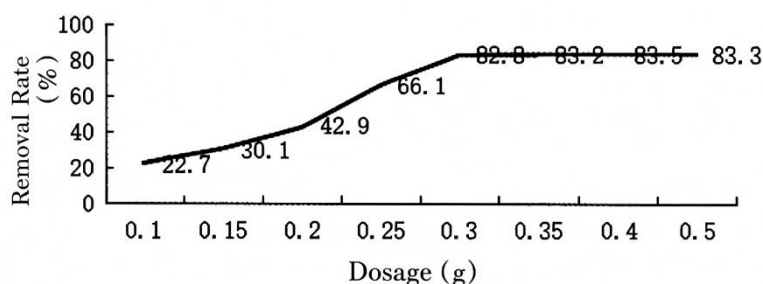


Figure 5 Effect of dosage on removal rate

### 3.6. Effect of temperature on removal rate

In a 150 mL conical flask, 50 mL phenol solution with a concentration of 50 mg/L and 0.3 g modified  $\text{Fe}_3\text{O}_4$  nanoparticles were added. The effect of temperature on removal rate was determined by adjusting experimental temperature, and the experimental results are shown in Figure 6. It can be observed from Figure 6 that the removal rate increases first and then decreases with rising temperature. This may be because the increase in temperature at the initial stage improves the activity of the adsorbent and enhances the adsorption performance. When the temperature exceeds 45 °C, the exothermic adsorption process is adversely affected by excessively high ambient temperature.

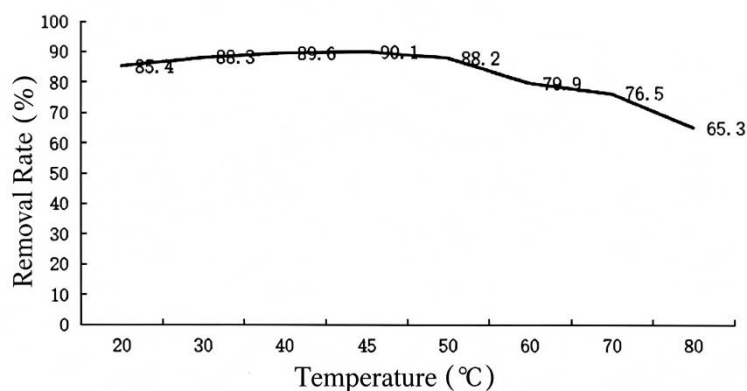


Figure 6 Effect of reaction temperature on removal rate

### 3.7. Effect of initial concentration on removal rate

In a 150 mL conical flask, 50 mL phenol solutions of different concentrations and 0.3 g modified  $\text{Fe}_3\text{O}_4$  nanoparticles were added. The influence of initial phenol concentration on the removal rate was investigated by adjusting the initial phenol concentration, and the results are shown in Figure 7. As illustrated in Figure 7, the removal rate remains stable at first and then decreases with the increase of initial concentration. It indicates that the adsorbent exhibits favorable adsorption performance at low concentrations. Once the concentration exceeds the adsorption capacity, the adsorption removal rate drops rapidly. An initial concentration of 50 mg/L was adopted in this experiment.

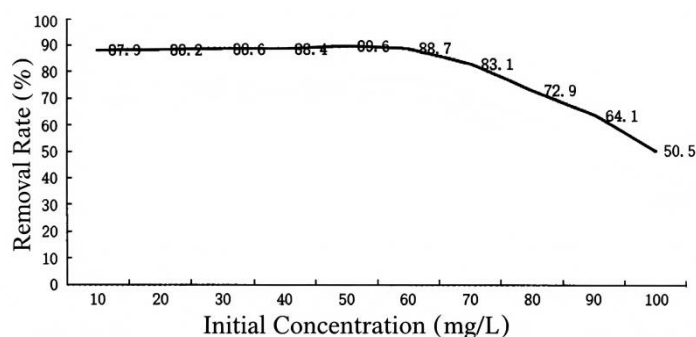


Figure 7 Effect of initial concentration on removal rate

### 3.8. Recycling experiment

After the amino-modified  $\text{Fe}_3\text{O}_4$  reached adsorption saturation, the adsorbent was separated and regenerated (heated at 90 °C for 60 min), followed by repeated utilization [6] - [7]. The results are shown in the table below. It can be seen that after six cycles of adsorption and regeneration, the decrease in phenol removal rate of the adsorbent is insignificant, with a total loss rate of approximately 2.6 %.

Table Effect of adsorbent regeneration on removal rate

| Regeneration cycles | Removal rate (%) | Regeneration cycles | Removal rate (%) |
|---------------------|------------------|---------------------|------------------|
| 1                   | 86.8             | 5                   | 84.9             |
| 2                   | 86.1             | 6                   | 84.2             |
| 3                   | 86.3             | 7                   | 77.4             |
| 4                   | 85.4             | 8                   | 56.6             |

## 4. Conclusions

After amino modification,  $\text{Fe}_3\text{O}_4$  achieves effective adsorption of phenol. Under the conditions of adsorbent dosage of 0.3 g, pH of 9, adsorption time longer than 15 min and temperature of 45 °C, the removal efficiency for 50 mL phenol solution of 50 mg/L exceeds 90 %. After six regeneration cycles of the adsorbent, the removal rate only decreases by 2.6 %.

## 5. References

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