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Microstructure and Heavy Metal Adsorption Properties of Citric Acid-modified Fe_3O_4 Adsorbents

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Abstract: Heavy metals such as copper, lead, and chromium in industrial wastewater are difficult to degrade naturally, and conventional treatment processes are prone to producing secondary pollutants. Magnetic ferroferric oxide (Fe_3O_4) materials can achieve rapid recovery through magnetic fields, and they have become popular materials for wastewater adsorption treatment. However, pure Fe_3O_4 particles are easy to agglomerate and lack sufficient effective adsorption sites. This study adopts a single ferrous salt precipitation oxidation process and uses citric acid as a modification auxiliary to prepare citric acid-modified Fe_3O_4 adsorbents. This study characterizes the micro-morphology, crystal structure, and pore parameters of the materials using SEM, XRD, and BET. It conducts comparative adsorption experiments using Cu^{2+} as the target heavy metal pollutant. Experimental data show that citric acid can slow down the grain growth rate through complexation, improve the dispersion degree of particles, and increase the specific surface area of materials. Nevertheless, citric acid will form an organic coating on the particle surface and occupy part of the hydroxyl active sites, so the final adsorption efficiency of the modified materials for Cu^{2+} is lower than that of unmodified Fe_3O_4 samples.

1. Introduction

1.1 Current Situation and Treatment Difficulties of Heavy Metal Water Pollution

China's current pollution reduction and carbon emission control standards continue to tighten. Wastewater discharged by the electroplating, metallurgy, and leather-making industries contains a large number of heavy metal ions, such as lead, chromium, and copper [1]. These heavy metals have stable chemical properties and cannot be decomposed by microorganisms. They will

accumulate in animals and plants along the food chain and eventually damage human kidneys and nervous systems. Conventional sewage treatment methods have obvious shortcomings [2]. The chemical precipitation method has low raw material costs, but it generates large amounts of hazardous sludge and incurs high subsequent disposal costs [3]. The membrane separation method can achieve excellent effluent quality, but operating the equipment consumes a large amount of energy [4]. Ion exchange resins have high procurement prices and are not suitable for large-scale sewage treatment. The adsorption method has simple operation and produces few solid wastes, so scholars have extensively studied it in recent years. Fe_3O_4 magnetic nanomaterials have inherent magnetism, and they can be quickly separated and recovered by magnets after sewage treatment. The materials can address the challenges of difficult recovery and loss associated with ordinary powder adsorbents, and they are ideal for advanced treatment of heavy metal wastewater.

1.2 Defects of Pure Fe_3O_4 Adsorption Materials

Fe_3O_4 nanoparticles prepared by conventional methods have two core problems. First, the particle surface has high surface energy, making particles prone to mutual adhesion and agglomeration during preparation. The accumulation of particles will block internal pores, greatly reduce the specific surface area of materials, and decrease the number of active sites that can capture heavy metals. Second, the grain growth rate is difficult to control, and the products will contain acicular and flaky miscellaneous crystals with irregular crystal structures and poor adsorption stability. Many researchers add organic auxiliaries to modify Fe_3O_4. Citric acid is a cost-effective modification reagent because it is non-toxic, readily soluble in water, capable of chelating with iron ions, regulating grain formation, and improving the dispersion of the powder.

1.3 Research Status of Citric Acid-modified Fe_3O_4 at Home and Abroad

Chinese scholars Wang Jiaqi et al. (2022) used citric acid to regulate the oxidation and precipitation process of ferrous ions and successfully prepared Fe_3O_4 powder with better dispersion [5]. Their experiments confirmed that citric acid can reduce grain size and optimize pore structure, but they did not systematically compare the adsorption performance of materials before and after modification. Li Li's research team (2020) verified by characterization methods that citrate radicals adsorb on the crystal surface, creating steric hindrance and inhibiting particle agglomeration. Still, excessive citric acid will cover surface active hydroxyl groups and reduce the heavy metal adsorption capacity of materials [6].

Foreign Mustafa's team (2025) adopted the sol-gel method combined with citric acid modification to obtain Fe_3O_4 materials with developed pores, and the materials showed good adsorption potential for copper ions [7]. However, the sol-gel process requires high-temperature calcination, which leads to high costs and is not suitable for batch production. Most existing studies only analyze the microstructural optimization effect of citric acid, and few studies simultaneously compare the microscopic characteristics and adsorption performance of materials prepared by modified, unmodified, and solid-phase methods. This study fills the experimental gap in this field.

1.4 Research Objectives and Contents

1.4.1 Research Objectives

This study uses single ferrous sulfate as the raw material. It sets up three groups of control samples: solid-phase ball-milled Fe_3O_4 BM, citric acid-free single ferrous precipitation oxidation Fe_3O_4 Schikorr, and citric acid-assisted modified Fe_3O_4 CA (2).

The experimental objectives are divided into three points:

First, this study analyzes the regulatory effect of citric acid on the grain morphology, crystal purity, specific surface area, and pore-size distribution of Fe_3O_4.

Second, this study compares the adsorption rates and equilibrium adsorption efficiencies of the three materials for Cu^{2+} in water and explains the correlation between microstructure and adsorption performance.

Third, this study clarifies the advantages and limitations of citric acid modification in this experimental system and screens low-cost synthesis processes suitable for heavy metal wastewater treatment.

1.4.2 Research Contents

First, this study prepares three types of magnetic Fe_3O_4 adsorbents using three processes and documents the complete experimental procedures.

Second, this study completes the characterization of the materials' microstructure using Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and a Brunauer-Emmett-Teller (BET) specific surface area analyzer.

Third, this study conducts static Cu^{2+} adsorption experiments and records adsorption rate data at different time points.

Fourth, this study analyzes the dual-action mechanism of citric acid, combines it with characterization data and adsorption results, and proposes process optimization suggestions.

2. Experimental Sections

2.1 Experimental Reagents

All experimental reagents in this study are analytical grade (AR). The detailed reagent information is shown in Table 1.

Table 1: Details of Experimental Reagents

Reagent Name	Chemical Formula	Manufacturer
Ferrous Sulfate Hexahydrate	$FeSO_4 \cdot 6H_2O$	Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd.
Sodium Hydroxide	NaOH	Tianjin Yongda Chemical Reagent Co., Ltd.
Citric Acid	$C_6H_8O_7$	Tianjin Ruijinte Chemicals Co., Ltd.
Reduced Iron Powder	Fe	Tianjin Yongda Chemical Reagent Co., Ltd.
Anhydrous Ethanol	C_2H_5OH	Tianjin Yongda Chemical Reagent Co., Ltd.
Sodium Acetate Trihydrate	$CH_3COONa \cdot 3H_2O$	Tianjin Ruijinte Chemicals Co., Ltd.

2.2 Experimental Instruments

The experimental instruments include an FA1004B electronic analytical balance, DF-101S digital constant temperature magnetic stirrer, WHL-25A electric constant temperature drying oven, permanent magnet for magnetic separation, planetary ball mill, JSM-7800F thermal field emission scanning electron microscope, D8 ADVANCE X-ray diffractometer, and BSD-660S BET specific surface area analyzer.

2.3 Preparation Methods of Three Kinds of Fe_3O_4 Samples

2.3.1 Solid-phase Ball Milling Method (Fe_3O_4 BM)

The experimental principle relies on mechanical force to induce chemical reactions. Iron powder undergoes oxidation under the action of grinding impact and extrusion, thereby directly generating Fe_3O_4. The core reaction equations are as follows:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2\uparrow \text{ (Mechanical grinding)} \quad (1)$$

$$6Fe + 4O_2 = 2Fe_3O_4 \text{ (Mechanical grinding)} \quad (2)$$

Operation steps: Researchers weigh the reduced iron powder, mix it with water to prepare a slurry, and load the slurry into a ball-milling tank with grinding balls for sealing. After prolonged high-energy grinding, researchers separate the black solids using a magnet, repeatedly wash them with deionized water, and dry them at 80℃ to obtain solid-phase Fe_3O_4 powder [8].

2.3.2 Single Ferrous Salt Precipitation Oxidation Method (Fe_3O_4 Schikorr)

This method uses only ferrous sulfate as the single iron source, oxidizes divalent iron by introducing air in an alkaline environment, and synthesizes Fe_3O_4 in one step. The main reaction equation is as follows:

$$6Fe(OH)_2 + O_2 = 2Fe_3O_4 + 6H_2O \quad (3)$$

Operation steps: Researchers prepare a 0.05 mol/L ferrous sulfate solution (solution A) and an alkaline sodium hydroxide solution (solution B). Researchers stir solution A at a constant temperature, slowly add an alkaline solution to adjust the pH, and continue stirring for 15 minutes. When the solution changes from dark green to black, researchers magnetically separate and wash the precipitate, and dry the precipitate to obtain unmodified Fe_3O_4 samples [9].

2.3.3 Citric Acid-assisted Modified Precipitation Oxidation Method (Fe_3O_4 CA (2))

Citric acid ionizes citrate radicals in the solution, and citrate radicals form soluble complexes with Fe^{2+} and Fe^{3+} to delay the rapid precipitation of crystals. The reaction equations are as follows:

$$C_6H_8O_7 \rightleftharpoons C_6H_5O_7^{3-} + 3H^+ \quad (4)$$

$$Fe^{2+} + 2Fe^{3+} + 8OH^- = Fe_3O_4\downarrow + 4H_2O \quad (5)$$

Operation steps: Researchers dissolve ferrous sulfate, citric acid, and sodium acetate in deionized water to prepare solution A, then stir the solution at a constant temperature. Researchers drop sodium hydroxide alkaline solution at a constant speed, finish dropping within 30 minutes, and continue stirring for 1 hour. Researchers perform magnetic separation, wash the precipitate to neutrality, and dry the precipitate at 80℃ for 8 hours to obtain citric acid-modified Fe_3O_4 CA (2).

2.4 Material Characterization Methods

First, SEM (scanning electron microscopy): Researchers observe particle morphology, size, and degree of agglomeration at a magnification of 50,000× with a unified scale of 100nm.

Second, X-ray Diffraction (XRD): The scanning range is $2^{\theta} = 15 \sim 85°$ to analyze the crystal phase and crystallization purity of materials.

Third, BET nitrogen adsorption: Researchers measure the specific surface area and average pore radius of materials to assess the degree of pore development.

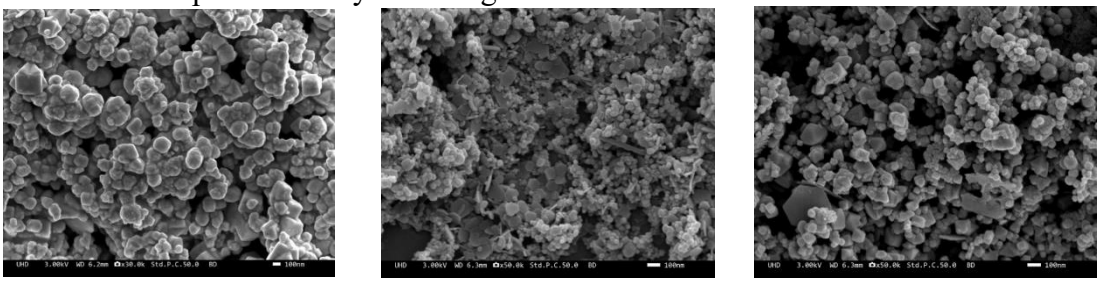
2.5 Heavy Metal Cu^{2+} Adsorption Experiment

Researchers prepare a copper sulfate solution at a fixed concentration to simulate copper-containing wastewater and add three types of Fe_3O_4 adsorption materials to the solution. The experiment sets adsorption time gradients of 3 min, 6 min, 10 min, 20 min, 30 min, and 60 min. After reaching the designated time, researchers quickly separate the supernatant using a magnet, measure the residual Cu^{2+} concentration, and calculate the adsorption rate [10].

3. Results and Analysis

3.1 Effect of Citric Acid Modification on Micro-morphology (SEM Analysis)

Fe_3O_4 samples prepared via three different fabrication processes exhibit significant differences in microscopic morphology, particle size, and dispersion performance. The SEM image characteristics of the three Fe_3O_4 samples are analyzed in Figure 1.



Fe_3O_4 BM Samples Fe_3O_4 Schikorr Samples Fe_3O_4 CA(2) Samples

Figure 1: SEM Images of Three Fe_3O_4 Samples

The SEM morphology of the three samples has obvious differences, which directly reflects the regulatory effect of citric acid.

First, the Fe_3O_4 BM sample prepared by the solid-phase method has a wide particle size range of about 100nm. The grains have sharp edges and corners, and mechanical grinding causes hard agglomeration and particle welding. The degree of dispersion of the sample is only 5%~10%, with dense grain stacking and few internal pores.

Second, the unmodified Fe_3O_4 Schikorr sample has a grain size of less than 50nm with complete cubic and octahedral crystal forms and smooth particle surfaces. The sample shows only slight soft agglomeration, with a dispersion degree of 15% and uniform, ordered grain growth.

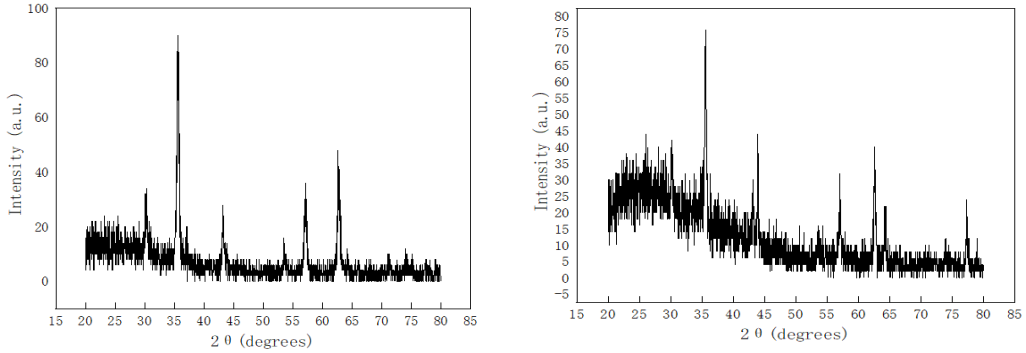
Third, the citric acid-modified Fe_3O_4 CA (2) sample has a grain size of 40~60nm with the narrowest particle size distribution. The adhesion between particles is greatly reduced, and the degree of dispersion is increased to 20%. Citrate radicals adsorb on the grain surface to generate electrostatic repulsion, inhibit the irregular agglomeration of grains, and solve the serious agglomeration problem of pure Fe_3O_4 particles.

Samples without citric acid, when dropwise added in the early improvement stage, generate acicular β-FeOOH crystals of miscellaneous types. After process optimization with uniform alkaline solution dropwise addition and an increased reaction temperature, miscellaneous crystals largely disappear, and the products are dominated by pure cubic Fe_3O_4 grains. The result demonstrates that citric acid, under appropriate reaction conditions, can stably regulate grain morphology.

3.2 Crystal Phase Analysis (XRD Patterns)

This study explores the effects of citric acid modification on the crystal phase, crystallinity, and

purity of Fe_3O_4. XRD tests and analyses are performed on unmodified and modified samples. The XRD pattern characteristics of the samples are displayed in Figure 2.



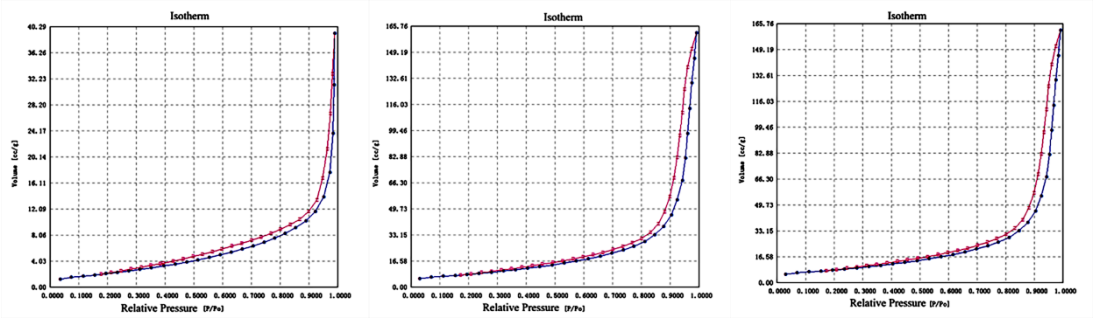
Fe_3O_4 Schikorr Samples Fe_3O_4 CA(2) Samples

Figure 2: XRD Patterns of Fe_3O_4 Schikorr and Fe_3O_4 CA(2) Magnetic Materials

Fe_3O_4 Schikorr and Fe_3O_4 CA (2) samples have consistent XRD pattern characteristics. Standard Fe_3O_4 characteristic diffraction peaks appear at 2^{θ}=30.1 °, 35.5 °, 43.2 °, 57.0 °, and 62.6 °, which correspond to (220), (311), (400), (511), and (440) crystal planes, respectively. The peaks are sharp without miscellaneous peaks, which indicates high crystallization purity. The citric acid-modified sample shows no miscellaneous peaks of iron citrate and iron oxide. The result indicates that citric acid adsorbs only on the crystal surface and does not alter the main crystal structure of Fe_3O_4 or destroy the target crystal phase.

3.3 Pore Structure and Specific Surface Area (BET Isotherms)

The specific surface area and pore structure parameters of the three samples can directly reflect differences in their microscopic structures. The BET adsorption isotherms of Fe_3O_4 samples prepared by three different processes are shown in Figure 3.



Fe_3O_4 BM Samples Fe_3O_4 Schikorr Samples Fe_3O_4 CA(2) Samples

Figure 3: BET Adsorption Isotherms of Three Fe_3O_4 Samples

The summary of BET test data of the three materials is as follows:

First, Fe_3O_4 BM has a specific surface area of 8.605m²/g and an average pore radius of 14.2nm. Tight agglomeration of particles caused by solid-phase grinding blocks internal pores, so the sample has the minimum specific surface area.

Second, Fe_3O_4 Schikorr has a specific surface area of 30.525m²/g and an average pore radius of 16.48nm. Grains prepared by the liquid-phase precipitation method have good dispersion and developed mesoporous structures.

Third, Fe_3O_4 CA (2) has a specific surface area of 37.615m²/g and an average pore radius of 16.88nm. Citric acid improves particle dispersion and increases the number of internal pores,

resulting in the sample having the highest specific surface area among the three groups.

All three curves belong to type I mesoporous material isotherms. The nitrogen adsorption capacity increases rapidly in the medium and high-pressure region, which proves that a large number of mesoporous channels exist inside the materials. Citric acid modification effectively broadens pores and increases specific surface area, so it can theoretically provide more adsorption sites. However, the actual adsorption performance does not improve synchronously, and the internal reasons will be explained below.

3.4 Comparison of Cu^{2+} Adsorption Performance of Three Materials

The adsorption experimental data are presented as a line chart in Figure 4. The overall adsorption efficiency ranking of the three materials is: Fe_3O_4 Schikorr (unmodified) > Fe_3O_4 CA (2) (citric acid-modified) > Fe_3O_4 BM (solid-phase ball milling).

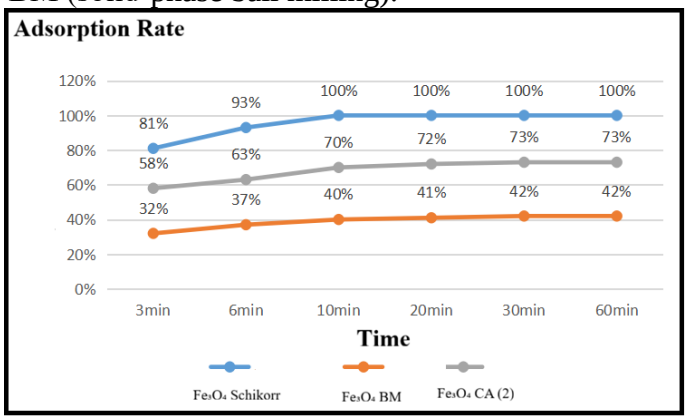


Figure 4: Adsorption Performance of Materials Synthesized via Different Methods

First, the solid-phase sample has an adsorption rate of only 32% at 3min and an equilibrium adsorption rate of 42% at 60min. Serious particle agglomeration and a small specific surface area lead to insufficient effective adsorption sites and the worst adsorption capacity.

Second, the citric acid-modified sample has an adsorption rate of 58% at 3min and an equilibrium adsorption rate of 73% at 60min. Although the material has the highest specific surface area, the carboxyl groups of citrate radicals chelate with hydroxyl groups on the Fe_3O_4 surface, forming an organic thin film on the outer layer of the grains. The film covers a large number of hydroxyl active sites that can bind Cu^{2+} and offsets the advantages brought by the high specific surface area.

Third, the unmodified single ferrous precipitation sample has an adsorption rate of 81% at 3min and reaches a stable adsorption rate of 100% at 20min. A large number of exposed -OH groups on the grain surface can quickly capture Cu^{2+} through complexation and electrostatic interactions, thereby yielding the optimal adsorption rate and equilibrium capacity.

3.5 Dual Action Mechanism Analysis of Citric Acid Modification

Citric acid has both positive and negative effects in the Fe_3O_4 synthesis system, and this conclusion is the core of this experiment.

3.5.1 Positive Optimization Effect (Improving Microstructure)

First, complexation slow-release effect: Citrate radicals combine with free Fe^{2+} in the solution to form soluble complexes, reduce the concentration of free iron ions, slow down the rapid

precipitation of crystal nuclei, and avoid the stacking and agglomeration of a large number of grains in an instant.

Second, steric hindrance effect: Citrate radicals adsorb on the surface of newly formed grains, and negatively charged groups generate electrostatic repulsion to increase the spacing between particles, improve dispersion, and increase the specific surface area of materials.

Third, miscellaneous crystal inhibition effect: Citric acid combined with uniform alkaline solution dropwise addition stabilizes the system pH, reduces the generation of acicular β-FeOOH and flaky α-Fe_2O_3 impurities, and improves product purity.

3.5.2 Negative Restriction Effect (Reducing Adsorption Performance)

Citric acid molecules contain three carboxyl groups, which will preferentially bind to unsaturated hydroxyl sites on the Fe_3O_4 surface to form a stable coating layer. Cu^{2+} in water also relies on hydroxyl complexation to complete adsorption. The organic coating layer will block the contact between Cu^{2+} and the material surface and directly reduce the heavy metal adsorption capacity of the material. Adjusting the citric acid addition ratio or adding subsequent desorption and cleaning steps to remove excess surface citric acid can balance the high-dispersion microstructure with high adsorption efficiency, which is a future direction for process optimization.

4. Conclusions

First, in terms of microstructure, citric acid-assisted modification can significantly optimize the grain morphology of Fe_3O_4. Modified grains have a uniform size and improved dispersion, and the specific surface area of the modified material reaches 37.615 m^2/g, which is much higher than that of solid-phase and unmodified samples. XRD results show that citric acid does not alter the cubic crystal phase of Fe_3O_4, and the product is highly pure.

Second, in terms of adsorption performance, under the fixed citric acid addition amount in this experiment, the adsorption efficiency of the citric acid-modified sample for Cu^{2+} is 73%, which is lower than the 100% adsorption efficiency of the citric acid-free single ferrous salt precipitation sample. Citric acid forms an organic coating layer on the particle surface, occupies hydroxyl active sites, and weakens the heavy metal capture capacity of the material. The solid-phase ball-milled sample exhibits severe agglomeration, with an equilibrium adsorption rate of only 42% and the worst overall performance.

Third, regarding process selection, the citric acid-assisted precipitation oxidation method is suitable for preparing high-dispersion, high-specific-surface-area magnetic Fe_3O_4 powder for biomedical and carrier material applications. The citric acid-free single ferrous salt precipitation oxidation process is preferred for the adsorption treatment of heavy metal wastewater. This process has regular crystal morphology, sufficient active sites, a fast adsorption rate, and low raw material cost, and it is suitable for advanced treatment of industrial wastewater.

Fourth, in terms of research prospects, subsequent experiments can adjust the amount of citric acid added in a graded manner to explore whether low-dose citric acid can improve dispersion without excessively covering adsorption sites. Meanwhile, researchers can carry out material cycle regeneration experiments to verify the performance attenuation law of citric acid-modified Fe_3O_4 after repeated use.

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