

Synthesis of Hollow Spheres of Fe₂O₃ Using Vanadium Extraction Tailings for Removal of Methyl Orange Dyes

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Using vanadium extraction tailings as an iron source and glucose as a template, hollow spheres of Fe₂O₃ were successfully synthesized via hydrothermal synthesis for methyl orange adsorption treatment. The phase and structure of the samples were characterized by XRD, SEM, BET, and TEM. The results showed that the synthesized Fe₂O₃ exhibited a single hematite phase with a diameter of about 0.8–1.2 μm, the sphere wall was composed of nanoparticles and the specific surface area was 21.327 m²/g. The adsorption results showed the optimal conditions for methyl orange (MO) adsorption: for 1.0 g/L of adsorbent and a reaction time of 4 h, the MO adsorption rate was 85.9 % and the MO adsorption capacity of HSF was much higher than that of traditional Fe₂O₃.

Keywords: vanadium extraction tailings, hollow spheres of Fe₂O₃, methyl orange removal, synthesis.

1. INTRODUCTION

Waste water, which has a high concentration of harmful substances, can seriously threaten the environment and the health of the human population. Methyl orange (MO) is a typical pollutant in dye wastewater; the treatment of MO has been widely studied. In recent years, because iron oxide nanomaterials [1, 2] can provide extraordinarily vast activated surface area and robust stability while offering inexpensiveness, natural abundance, and environmentally friendly properties, there has been steady growth of research interest in developing iron oxide nanomaterials to remove dye pollutants [3] from contaminated water.

Iron oxide (Fe₂O₃) has enormous potential to be widely used in water treatment. Conventional methods of preparing Fe₂O₃ use a variety of Fe sources such as FeCl₃ [4], ferrocene [5], Fe(NO₃)₃ [6], and so on. The high cost of reagent-grade chemicals limits the scale of the application of Fe₂O₃. In order to reduce the preparation cost of Fe₂O₃, a low-cost source of Fe is needed.

One alternative Fe source, vanadium extraction tailings (VET), are the residue of vanadium slags after vanadium extraction for the chemical industry. In China, 3×10⁴ tons per year of VET have been produced, but have not been effectively utilized [7]. With the potential to create high value-added products and reduce environmental pollution, VET can be used to prepare building materials and ceramics and for leaching valuable elements [7–9].

Based on these features, VET was investigated as a low-cost and environmentally friendly starting material for the synthesis of hollow spheres of Fe₂O₃ (HSF). The use of HSF in adsorption for wastewater treatment was also studied.

2. EXPERIMENTAL DETAILS

The VET were obtained from the Jianlong Iron and Steel Group Corporation in China. Table 1 shows the chemical composition of the VET, indicating that the content of Fe₂O₃ was 46.52 % (analyzed by XRF, Shimadzu Analytical Instrument XRF-1800). All other chemicals used were analytical grade.

The Fe leaching experiments were carried out in an oil batch reactor. First, 30 g of VET was put into 300 ml HCl (1:1 volume ratio) at 373 K for 3 h under constant stirring. Next, the leaching solution was filtered from the mixture. The Fe content of the leaching solution was 43.54 g/L.

In the synthesis procedure of the hollow spheres of Fe₂O₃, glucose (40.0 mmol) was dissolved in deionized water for 1 h. The leaching solution from the VET was put into the glucose solution and stirred for 1 h. The final molar composition of the gel was glucose: Fe = 5:1. The solution was treated in an autoclave at 180 °C for 15 h. The gel was centrifugally separated to obtain the HSF precursor. The HSF precursor was dried at 80 °C for 4 h. Finally, the HSF were prepared at 600 °C for 3 h.

In the synthesis procedure of traditional Fe₂O₃, FeCl₃ was dissolved in deionized water for 1 h. The solution was then treated in an autoclave at 180 °C for 15 h. The gel was centrifugally separated and dried at 80 °C for 4 h.

Phase characterization of the samples was determined by X-ray diffraction (XRD, Rigaku D/max- RB) with Cu K radiation. Morphology of the samples was analyzed by scanning electron microscopy (SEM, Hitachi S-3400N) and transmission electron microscopy (TEM, FEI-F20). Surface area was determined by a surface area and porosity analyzer (BET, Quantachrome Instruments NOVA4000e). The liquor sample was analyzed via ICP-AES (Perkin-Elmer 3000 XL). The adsorption efficiency of HSF was assessed for MO dyes using a thermostated mechanical shaker.

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Table 1. Composition of VET (wt.%)

Compound	Fe ₂ O ₃	MnO	SiO ₂	Cr ₂ O ₃	V ₂ O ₅	Na ₂ O	TiO ₂	Al ₂ O ₃	MgO	CaO	Other
Content	46.52	7.79	15.76	5.59	1.55	5.01	8.98	2.21	2.46	2.85	1.28

The temperature and shaking speed for all adsorption experiments were kept constant at 30.0 ± 0.2 °C and 120 rpm, respectively. Typically, 50 ml of MO solution (20.0 mg/L) was mechanically shaken with varying amounts of HSF (0.4 – 1.2 g/L). The concentration of residual MO was measured by the UV–Vis spectrophotometer method at 665 nm. Eq. 1 can be applied to calculate the adsorption efficiency of MO.

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of the MO solution (g/L).

3. RESULTS AND DISCUSSION

XRD patterns of the HSF precursor and of the precursor heated at 600 °C for 3 h are presented in Fig. 1. Notably, no characteristic peaks of Fe₂O₃ structure can be found in Fig. 1 a, which implies that the precursor is composed of amorphous molecular of carbon and iron. In Fig. 1 b, all diffraction peaks can be indexed to pure-phase Fe₂O₃ according to the JCPDS (33-0664). No peaks of any other phase were detected, implying that a single hematite phase was produced in the system.

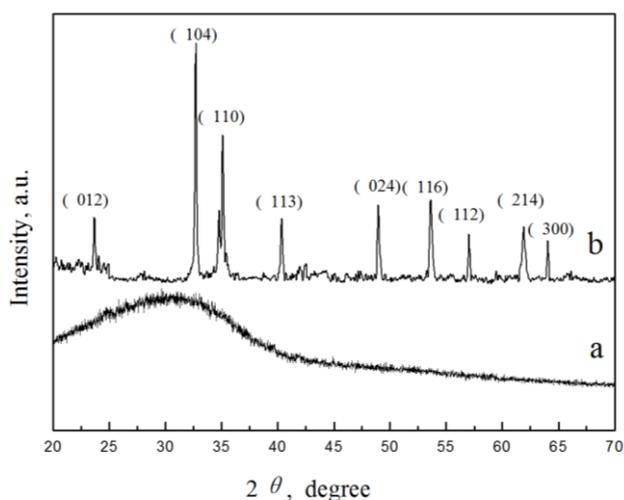


Fig. 1. XRD patterns: a – of HSF precursor; b – of HSF precursor heated at 600 ° for 3 h

Fig. 2 a is the SEM micrograph of the precursor particles; it indicates that the precursor consisted of spherical particles with a diameter of about 1.0–1.5 μm. In Fig. 2 b, the SEM micrographs indicate that the precursor heated at 600 °C for 3 h consisted of hollow particles with a diameter of about 0.8–1.2 μm. As shown in the inset of Fig. 2 b, the particle size and hollow features were further confirmed at lower magnification. Meanwhile, in Fig. 2, the shrinking and densification of the HSF diameter compared to the precursor reveal that Fe ions had little

influence on the diameter of particles in the heating process.

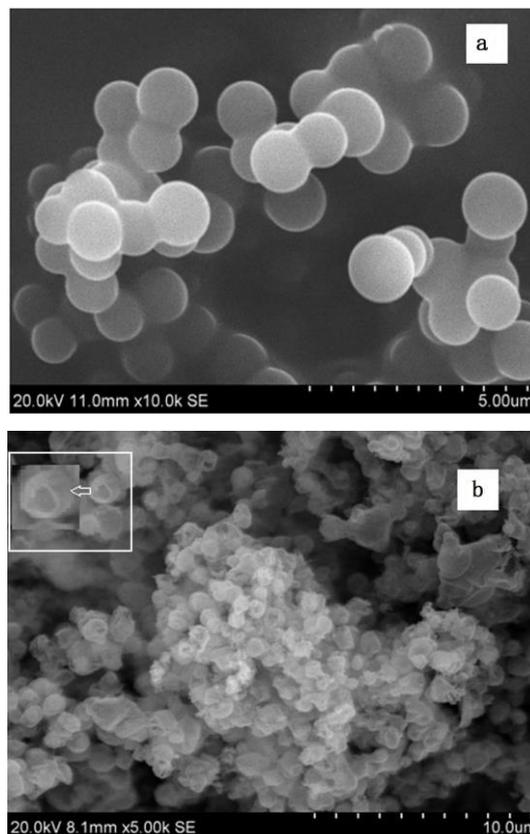


Fig. 2. SEM patterns: a – HSF precursor; b – of HSF precursor heated at 600 °C for 3 h

TEM patterns of HSF precursor heated at 600 °C for 3 h are shown in Fig. 3.

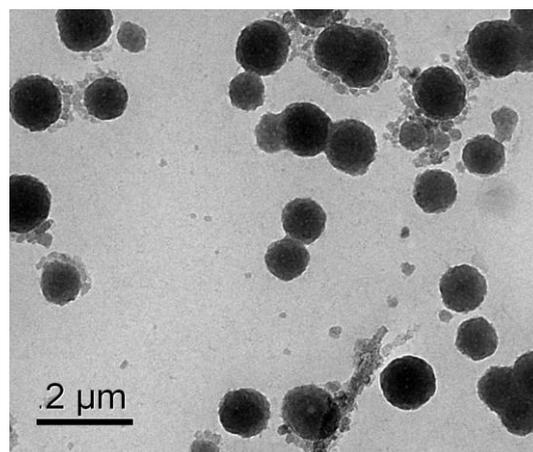


Fig. 3. TEM patterns of HSF

The TEM pattern shows that the sample forms a hollow sphere microstructure, and that the sphere wall is composed of nanoparticles. Fig. 4 shows the N₂

adsorption–desorption isotherms of HSF. The clear hysteresis loops revealed that the isotherms were type IV adsorption isotherms with an H3-type hysteresis loop. The BET specific surface area of HSF was 21.327 m²/g, the median pore diameters estimated was at ca. 3.021 nm. It also proves that the sphere wall is composed of nanoparticles and the pore diameters of nanoparticles is 3.021 nm.

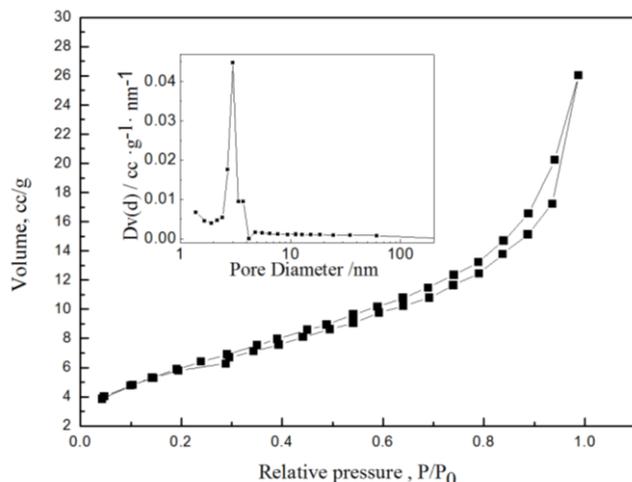


Fig. 4. N₂ adsorption–desorption isotherms of HSF

A possible forming process of HSF is shown schematically in Fig. 5. The carbon spheres could be synthesized from carbonification of glucose via hydrothermal treatment at 180 °C. It has been reported that glucose begins to aromatize and carbonize when the temperature is higher than that needed for normal glycosidation [10]. Then the iron ions can be adsorbed into the surface layer of the carbon spheres due to chelation between the hydroxyl, carboxyl and iron ions. Carbon was removed and iron oxide gradually formed after heat treatment at 600 °C for 3 h.

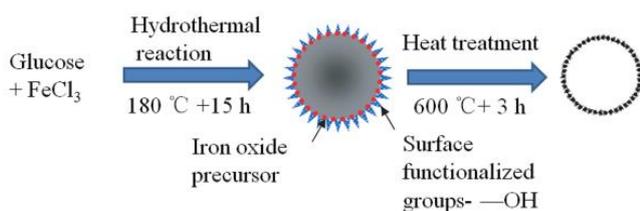


Fig. 5. Schematic illustration of the formation of HSF

Fig. 6 shows the adsorption efficiency of MO(*R*) by Fe₂O₃ as an adsorbent with varied content and reaction time. It can be seen that *R* increased with the reaction time from 1 to 4 h and reached a plateau at 4 h. With further increase of the adsorbent reaction time, *R* increased unobviously. As shown in Fig. 6 (from line (b) to line (f)), *R* increased rapidly with the increase of HSF content from 0.4 to 1.2 g/L at 4 h, then increased unobviously when the content of HSF exceeded 1.2 g/L. Comparing line (a) with lines (b) through (f) in Fig. 6, the MO adsorption capacity of HSF is much higher than that of traditional Fe₂O₃.

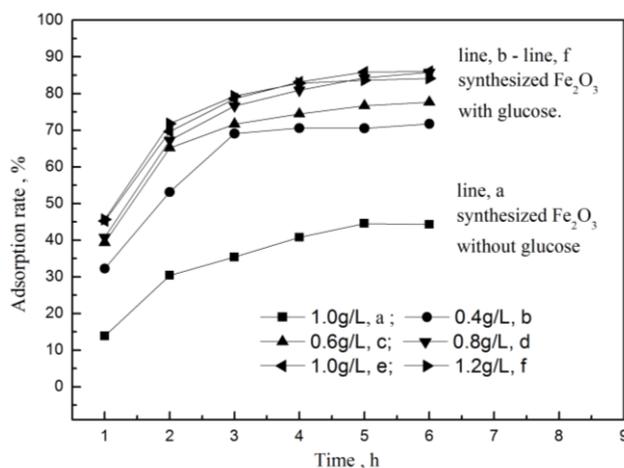


Fig. 6. Adsorption of MO onto Fe₂O₃ as a function of adsorbent content

4. CONCLUSIONS

In this study, HSF were synthesized using VET as a low-cost and environmentally friendly starting material. XRD results proved that the synthesis of HSF formed a single hematite phase. SEM results showed that the diameter of HSF is about 0.8–1.2 μm. The shrinking and densification of the diameter of HSF compared to the precursor reveal that Fe ions had little influence on the diameter. The walls of the hollow spheres were composed of nanoparticles, as TEM analysis showed, and the specific surface area of HSF was 21.327 m²/g.

The adsorption results showed that MO adsorption increased with the increase of reaction time from 1 to 4 h and the dosage of HSF from 0.4 to 1.2 g/L. The optimal conditions for MO adsorption were 1.0 g/L of adsorbent and reaction time of 4 h, which resulted in an MO adsorption rate of 85.9%. Furthermore, the MO adsorption capacity of HSF is much higher than that of traditional Fe₂O₃.

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