

Characterization and Application of Adsorption Material with Hematite and Polystyrene

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ABSTRACT

In this study, a three-dimensional ordered macroporous hematite was prepared using the polystyrene colloid crystal templates and characterized by X-ray diffraction, scanning electron microscope, transmission electron microscope, and nitrogen adsorption isotherm. The as-prepared hematite shows a porous structure consisting of the macropores about 200 nm in diameter and the walls about 20 nm in thickness. The adsorption of Pb²⁺ and Cd²⁺ ions in aqueous solution by this hematite was also evaluated. At room temperature, each gram hematite adsorbs 12.5 mg of Pb²⁺ ions and 7.0 mg of Cd²⁺ ions. The results suggest that the obtained hematite should be a promising adsorbent to remove Pb²⁺ and Cd²⁺ ions, and other heavy metal ions from aqueous solution.

Keywords: Macroporous, Heavy Metal Ions, Adsorption, Pollution

1. Introduction

With rapid development of economics all over the world, water pollution becomes a vital problem for people to survive in the earth because the heavy metal ions are detrimental to human health. Lead (Pb²⁺) and cadmium (Cd²⁺) ions are toxic heavy metal ions that can enter human body through inhalation and ingestion from a variety of sources such as contaminated air and water, soil and food [1,2]. The deposits of Pb and Cd compounds are difficult to be absorbed but people can absorb their soluble salts. Hence, it is very important for us to remove Pb²⁺ and Cd²⁺ ions from water for consideration of the health of human being. There are many articles discuss the elimination of Pb²⁺ [3-5] and Cd²⁺ [6-8] ions from aqueous solution. However, few of papers discuss the effect of three-dimensional ordered macroporous (3DOM) materials in water treatment.

Three dimensionally ordered macroporous (3DOM) materials, which consisting of a large number of macropores more than 100 nm in diameter and the walls less than 100 nm in thickness, have been used as carriers [9-13], adsorbents [14-17] and electrode materials [18-23]. As adsorbents, 3DOM materials with a large specific surface area and porosity are favorable to adsorption of the heavy metal ions. Because of being available in large quantity with relatively low cost, α -Fe₂O₃ (hematite) has

been widely used as an adsorbent to remove heavy metal ions from water [7,24-28]. However, few people have investigated the capability of the 3DOM α -Fe₂O₃ to remove Pb²⁺ and Cd²⁺ ions from aqueous solution.

Here we report the preparation of a 3DOM α -Fe₂O₃ material using polystyrene (PS) colloidal crystal template. Its porous structure was characterized by nitrogen adsorption isotherm plot, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs. Its adsorption capability of Pb²⁺ and Cd²⁺ ions in aqueous solution was investigated as well.

2. Experimental

Polystyrene colloidal crystal spheres were synthesized according to the method reported in the literature [29]. At first, 2.8 g polyvinylpyrrolidone (PVP K30, M_w = 30000, BASF) was dispersed in 200 ml deionized water forming micelles under mechanical stirring. Subsequently, 0.1 g K₂S₂O₈ and 21 g styrene were added to the polymeric solution. The mixed solution was deoxygenated by bubbling argon at room temperature for 1 h with gentle stirring, and then polymerized at 70°C for 24 h in an argon atmosphere. Finally, the synthesized mono-dispersed PS spheres were arrayed into the close packed colloidal crystals by centrifuge (2000 r·min⁻¹) for 24 h, and kept in air at 50°C for 48 h to evaporate the remaining water and alcohol.

To prepare the 3DOM hematite, Fe_2O_3 needs to be formed inside the template. First, the PS colloidal crystal template prepared above was soaked in the solution of $1.5 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 in glycol/methanol (3:2, by volume) for 8h. Then the solution was removed by filtration and the template saturated with FeCl_3 was dried at 50°C under vacuum for 10h to form the precursor. After that, the dried precursor was heated from room temperature to 500°C at a rate of $0.5^\circ\text{C}\cdot\text{min}^{-1}$, and calcined at 500°C for 10h in air. Finally, the porous hematite was obtained with elimination of the PS template.

Morphology of the prepared Fe_2O_3 particles was observed by Transmission electron microscope (TEM, JEOL JEM 2100) and scanning electron microscope (SEM, JSM-6360L). The crystalline structure was characterized by X-ray diffraction pattern recorded on a Rigaku D/max 2550 X-ray diffractometer. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves of the sample were recorded simultaneously on SDTQ 600 instrument ranged from ambient temperature to 750°C at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ under air. The specific area of the obtained Fe_2O_3 was measured using a Micromeritics Tristar ASAP 3000 BET apparatus.

Heavy metal ion adsorption of the prepared hematite was tested according to the literature [30]. 0.05 g of the adsorbent were added to a 50 ml aqueous solution of $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$ at 16.4 and $10.6 \text{ mg}\cdot\text{L}^{-1}$, respectively. The mixture was stirred for various times and then centrifuged at 6000 rpm for 15 min. The concentrations of Pb^{2+} and Cd^{2+} ions of the obtained clear solution were measured using UV-vis spectroscopy after the solution was adjusted to pH 2. Diphenylthiocarbazone and 1-(2-pyridinylazo)-2-naohtalenol were used as the chromogenic reagents for Pb^{2+} and Cd^{2+} ions, respectively.

3. Results and Discussion

Figure 1 shows the TG and DTA profiles of the precursor. The weak endothermic peak below 100°C can be assigned to the evaporation of the remaining methanol and water. The weight loss from 100°C to 250°C is attributed to the evaporation of the remaining glycol in the samples. The strong endothermic peaks in the temperature range of 250°C - 450°C result from the thermal decomposition of PS template and the formation of Fe_2O_3 nanoparticles. No obvious endothermic/exothermic peaks display above 450°C suggesting that the PS template should have decomposed completely and the pure Fe_2O_3 has formed.

Figure 2 shows the X-ray diffraction pattern of the Fe_2O_3 . The diffraction peaks of the as-prepared Fe_2O_3 agree very well with those reported in the literature[31], where Fe_2O_3 was indexed as the rhombohedral $\alpha\text{-Fe}_2\text{O}_3$

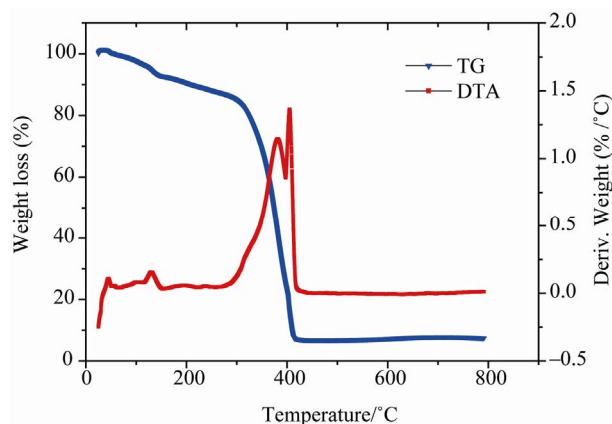


Figure 1. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) plots of the precursors at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ under air atmosphere from room temperature to 700°C .

[hematite: JCPDS 87-1166]. No other diffraction peaks of impurities such as Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ were observed. The high intensities of the diffraction peaks indicate that the prepared $\alpha\text{-Fe}_2\text{O}_3$ has a perfect crystallization after heated at 500°C for 10 h under air atmosphere.

Figure 3 shows the TEM micrographs of the $\alpha\text{-Fe}_2\text{O}_3$ particles. It can be seen that the $\alpha\text{-Fe}_2\text{O}_3$ particles have the porous structure with uniform pore size and display 3DOM morphology. The porous structure, as shown in **Figure 3**, consists of the macropores about 200 nm in diameter and the walls about 20 nm in thickness.

The nitrogen adsorption isotherm of the 3DOM $\alpha\text{-Fe}_2\text{O}_3$ is shown in **Figure 4**. It presents a type IV isotherm with hysteresis loop similar to that reported [32]. The specific surface area calculated by the Brunauer-Emmett-Teller (BET) method and the pore volume determined by the Barrett-Joyner-Halenda (BJH) approach are $24.14 \text{ m}^2\cdot\text{g}^{-1}$ and $0.053 \text{ cm}^3\cdot\text{g}^{-1}$, respectively.

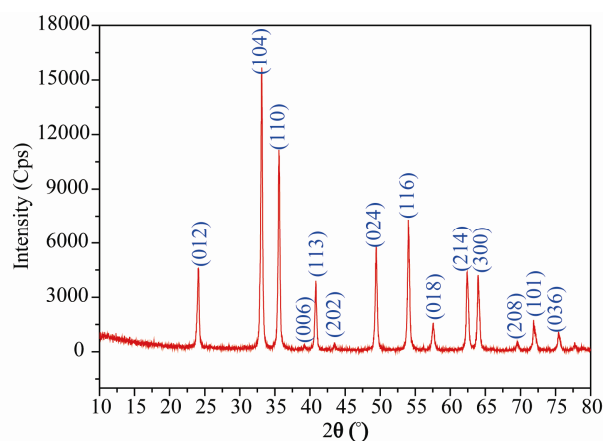


Figure 2. XRD pattern of the three-dimensional ordered macroporous $\alpha\text{-Fe}_2\text{O}_3$ material.

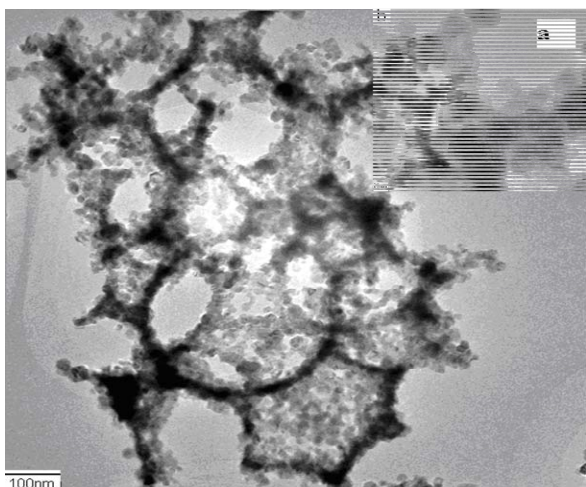


Figure 3. TEM (b) micrographs of the three-dimensional ordered macroporous α -Fe₂O₃ material.

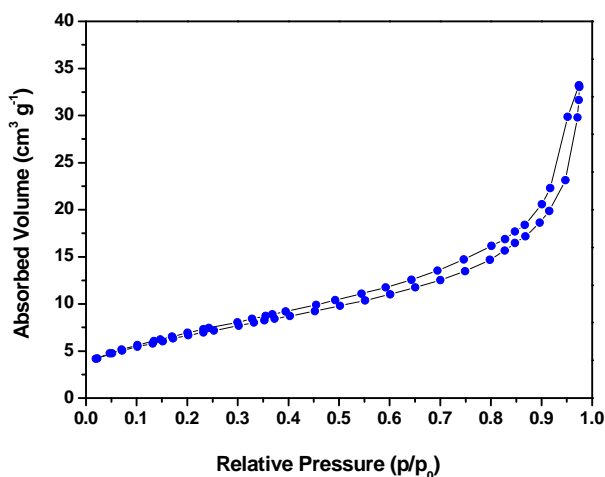
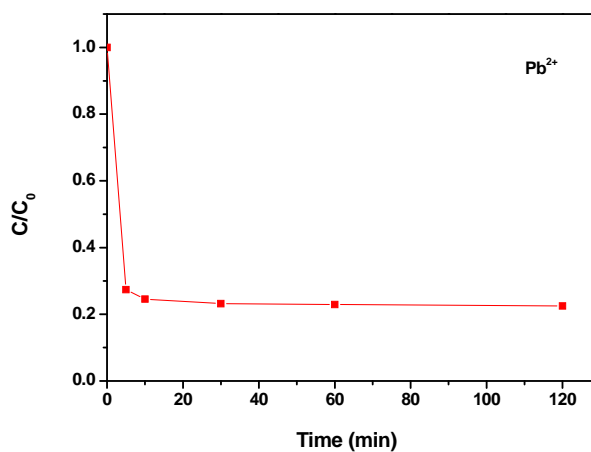
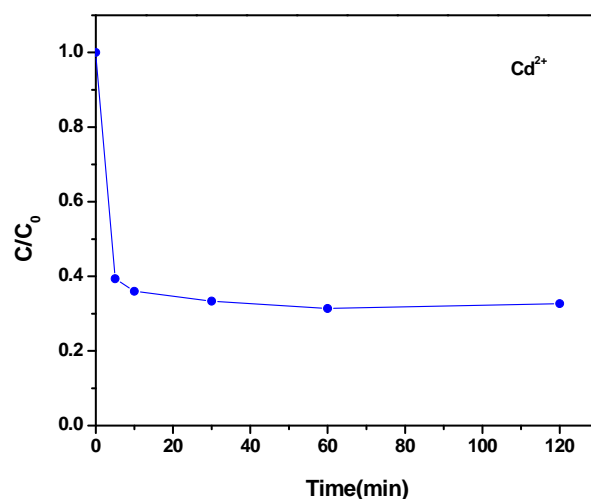


Figure 4. Nitrogen adsorption isotherm of the three-dimensional ordered macroporous α -Fe₂O₃ material.

Figure 5 shows the adsorption rates of Pb²⁺ (a), Cd²⁺ (b) ions on the 3DOM α -Fe₂O₃ material in aqueous solutions after various treatment times at room temperature. We can see that the concentrations of the metal ions decrease quickly after the addition of the 3DOM α -Fe₂O₃ adsorbent. The adsorption capacities of 3DOM α -Fe₂O₃ for Pb²⁺ and Cd²⁺ ions are 12.5 and 7.0 mg per gram of adsorbent, respectively. These values are higher than those of the hematite hollow spindles and microspheres [7], and similar to those of the ordered macroporous titanium phosphonate materials [33], but lower than those of the hybrid macroporous materials with thiol functional groups [15] and the activated carbons with larger specific surface area [34]. The data suggest that the 3DOM α -Fe₂O₃ material needs further improvement before it can be widely applied as adsorbent to remove the heavy metal ions from aqueous solution despite of its low cost.



(a)



(b)

Figure 5. Adsorption rates of Pb²⁺ (a), Cd²⁺ (b) ions on the three-dimensional ordered macroporous α -Fe₂O₃ material after various treatment times at room temperature.

4. Conclusions

The 3DOM α -Fe₂O₃ material was prepared using the PS colloid crystal template successfully and showed the porous structure, which is constructed with the 200-nm sized macropores and the 20-nm thick walls. Due to this special structure, its adsorption capacities of Pb²⁺ and Cd²⁺ ions in aqueous solution were 12.5 and 7.0 mg per gram adsorbent at room temperature, respectively. Compared with other adsorbents, the obtained 3DOM α -Fe₂O₃ material is inexpensive but it needs some further modifications for its wide application to remove heavy metal ions from aqueous solution.

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