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Preparation of NH_2 -Functionalized Fe_2O_3 and Its Chitosan Composites for the Removal of Heavy Metal Ions

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Abstract: $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{chitosan}$ ($\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$) with excellent physical properties and high adsorption capacities for several heavy metal ions were synthesized using a one-pot hydrothermal method. The materials were characterized by scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), transmission electron microscopy (TEM), and X-ray diffraction (XRD). Physicochemical properties were determined by the Fourier transform infrared spectra (FTIR) and nitrogen adsorption analysis (Brunauer–Emmett–Teller (BET) method). The results of the characterization studies show that the material is uniformly dispersed and has good crystallinity and well-defined porous particles. The material is mesoporous, and the particles have a specific surface area of $55.41\text{--}233.03\text{ m}^2\cdot\text{g}^{-1}$, a total pore volume of $0.24\text{--}0.54\text{ cm}^3\cdot\text{g}^{-1}$, and a diameter of $3.83\text{--}17.56\text{ nm}$. Additional results demonstrate that $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ are effective adsorbents for the removal of heavy metal ions from solution. In a ternary system, the order of their selective adsorption was determined to be $\text{Pb(II)} > \text{Cu(II)} > \text{Cd(II)}$, and the adsorption rate of Pb(II) was much higher than that of Cu(II) and Cd(II) . The metal ion adsorption capacity of $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ makes them promising adsorbents for wastewater cleanup.

Keywords: NH_2 -functionalized; $\gamma\text{-Fe}_2\text{O}_3$; Chitosan; heavy metal removal; biodegradable

1. Introduction

Toxic heavy metals can pose serious environmental problems and human health threats because of their persistent nature and high bioaccumulation potential [1,2]. Consequently, the development of effective materials for the remediation of toxic pollutants is important for the protection of public health [3].

Several methods have been developed to efficiently remove heavy metals from the environment; among these approaches are electrochemical technologies [4,5], adsorption [6,7], membrane filtration [8], and chemical precipitation [9,10]. In particular, adsorption is considered to be the most preferred technique because pollutants are not only relatively heat-stable but also resistant to oxidation and biodegradation. New functionalized adsorbents synthesized using different means have shown preferable adsorption capacities for heavy metals. Zhang [11] used a two-step process to synthesize chitosan–methyl acrylate–diethylenetriamine microspheres for the uptake of Pb(II) and

Cd(II). The results indicated that chitosan-methyl acrylate-diethylenetriamine microspheres had an outstanding ability to adsorb Pb(II) and Cd(II). Zhang [12] applied a simple glutaraldehyde crosslinking method and prepared a polyethyleneimine-functionalized Fe₃O₄/steam-exploded rice straw composite. The synthesized compound proved to be an effective adsorbent for the removal of Cr(VI) from wastewater. However, the above methods are often time-consuming and expensive, or the products are non-biodegradable.

Therefore, in the present work, we simplified the synthesis of functionalized NH₂-Fe₂O₃ and NH₂-Fe₂O₃/chitosan (NH₂-Fe₂O₃/CS), which a favorable adsorption capacity and good water solubility. The as-synthesized NH₂-Fe₂O₃ and NH₂-Fe₂O₃/CS adsorbents were characterized, and the as-prepared NH₂-Fe₂O₃ and NH₂-Fe₂O₃/CS were used as adsorbents to remove Pb(II), Cu(II), and Cd(II) from ternary solution. The removal rates of the metals by NH₂-Fe₂O₃/CS and NH₂-Fe₂O₃ had same order: Pb(II) > Cu(II) > Cd(II). From these results, NH₂-Fe₂O₃/CS and NH₂-Fe₂O₃ are expected to be prospective adsorption materials for heavy metal removal.

2. Materials and Methods

2.1. Synthesis of NH₂-Fe₂O₃

NH₂-Fe₂O₃ was synthesized by a one-pot hydrothermal technique. Solid FeCl₃·6H₂O (1.35 g) was added to 40 mL of ethylene glycol and anhydrous sodium acetate, after which it was stirred and dissolved. Then, 0.5, 1, 2, 3, and 4 mL of DETA and 0, 0.05, 0.10, 0.15, 0.20, and 0.25 g of sodium dodecyl sulfonate (SDS) were added at room temperature to form separate mixtures. The compound was placed into a Teflon-lined autoclave for calefaction at 160 °C for 8 h. After the material was cooled, it was rinsed with deionized water and ethanol. Finally, the sample was dried in an oven at a temperature below 60 °C.

2.2. Fabrication of NH₂-Fe₂O₃/CS

Deacetylated chitosan (CS) was mixed with 1% acetic acid, and NH₂-Fe₂O₃ prepared above was added to the mixture, followed by the cationic surfactant hexadecyltrimethylammonium bromide (CTAB). The compound was agitated for 2 h at 60 °C and then rinsed, oven-dried, and labeled as NH₂-Fe₂O₃/CS.

2.3. Sample Characterization

NH₂-Fe₂O₃ and NH₂-Fe₂O₃/CS were investigated by scanning electron microscopy (SEM; JSM-7001F), electron dispersive (EDS; AXIS ULTRA), transmission electron microscopy (TEM; JEM-2010), and X-ray diffraction (XRD; Bruker D8 ADVANCE) to measure the surface area, crystal characteristics, pore volume, and the pore diameter. The surface areas were determined from nitrogen sorption isotherms using Brunauer–Emmett–Teller (BET, Autosorb-iQ-MP-C) analysis. Fourier transformation infrared spectra (FTIR; VERTEX 70) were also analyzed in this study.

2.4. Heavy Metal Adsorption

Following the above analyses, 0.05 g of NH₂-Fe₂O₃ and 0.05 g of NH₂-Fe₂O₃/CS were weighed and suspended in a system of 10 mg·L^{−1} Pb(II), Cu(II), and Cd(II). The adsorption of a batch of samples was also tested in a system of Pb(II), Cu(II), Cd(II), and NaCl. The pH was adjusted to 5, and the mixtures were stirred at 35 °C for 2 h. Then, the concentrations were measured using ICP-MS. The same process was repeated three times.

3. Results and Discussion

3.1. Morphology of $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$

Images of $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ microspheres were recorded by SEM, which revealed the surface morphology and texture of each sample. Figure 1 a–f show $\text{NH}_2\text{-Fe}_2\text{O}_3$ after 8 h in the same conditions with different DETA volumes and $\text{SDS} = 0.1$ g. The composite material $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ is shown in supplemental Figure S1. More detailed structural information is observable in the TEM images (Figure 2 a–e).

Figure 1. SEM images of $\text{NH}_2\text{-Fe}_2\text{O}_3$ with different diethylenetriamine volumes (a–f indicate diethylenetriamine = 0.5, 1, 2, 3, 4, and 5 mL, respectively).

Figure 2. Transmission electron microscope images of $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ (a and b show $\text{NH}_2\text{-Fe}_2\text{O}_3$; c, d, and e show $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$).

The SEM images show that the $\text{NH}_2\text{-Fe}_2\text{O}_3$ product is granulated with a comparatively small size. With increasing volumes of DETA, the diameter of the particles decreases linearly (Figure 1). A comparison of these images shows that the $\text{NH}_2\text{-Fe}_2\text{O}_3$ molecules are scattered in the chitosan from the effects of anionic surfactant CTAB (see supplementary Figure S1 online). Because cetyltrimethylammonium bromide has a long hydrophobic alkyl chain, it not only facilitates dispersion but also enhances intercalation.

In the TEM images (Figure 2), both $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ are dispersed with good crystallization. The porous particles are clearly shown in Figure 2f.

When the quantity of DETA was constant and that of sodium dodecyl sulfate increased, the sample morphology was affected. Sodium dodecyl sulfonate decreases the interfacial energy of particles, and samples without the surfactant SDS were observed to be poorly dispersed. As the quantity of

SDS increased, the particle size initially increased and then decreased (see supplementary Figure S2 online). The composites were flat and smooth when the added SDS was between 0.05 and 0.1 g. When SDS = 0.2 g, the composite shape became triangular.

3.2. Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy spectra were another source of information used to characterize the materials. The characteristic peak at the wavelength of 560 cm^{-1} is attributed to the lattice vibration of the FeO_6 octahedron, namely, the elastic oscillation of the Fe-O bond [13]. The bands at 1443 cm^{-1} in Figure 3 are symmetrically stretched at Fe^{3+} and COO^- , while the bands at 1578 cm^{-1} are asymmetrically stretched. Figure 3a shows that these two positions have sharp bands that faded in the spectrum of $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$. This result is related to the highly active

Figure 3. FTIR of diverse DETA: (a) $\text{NH}_2\text{-Fe}_2\text{O}_3$ and its $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ composite; (b) $\text{NH}_2\text{-Fe}_2\text{O}_3$ with different volumes of DETA; (c) $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ with different volumes of DETA.

The peaks that are concentrated at 2927 and 2857 cm^{-1} in the spectrum are related to the hydrophobic alkyl groups in SDS and DETA. When the quantity of SDS is constant and the quantity of DETA increases, the bands at 2857 and 2927 cm^{-1} become larger. For the same quantity of DETA, an increase in SDS also slightly strengthens the peaks (Figure 4). The stretching of the O-H bond and N-H bond causes strong adsorption at 3425 cm^{-1} [14,15]. The presence of peaks at 1600 cm^{-1} indicates that the amino group is a component of the complex.

Figure 4. FTIR of $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ with varying quantities of sodium dodecyl sulfonate (SDS).

NH_2 group of chitosan. COO^- did not react with Fe^{3+} because of the limited DETA content (Figure 3b). With increasing DETA content, the band at 1578 cm^{-1} gradually decreases and finally vanishes when DETA = 2 mL.

3.3. Electron Dispersive Spectroscopy and X-ray Diffraction Analysis

The results of the electron dispersion spectroscopy and X-ray diffraction analyses indicate the phase and chemical composition of the synthesized materials. According to the standard card (JCPDS No. 39-1346), the peak intensity and width viewed in the XRD image represent a clear peak that is assigned to the crystal structure of $\gamma\text{-Fe}_2\text{O}_3$, as shown in Figure 5 [16,17]. The primary characteristic peaks of $\text{NH}_2\text{-Fe}_2\text{O}_3$ at $2\theta = 15.069^\circ, 30.38^\circ, 33.917^\circ, 44.484^\circ, 63.86^\circ, 64.875^\circ$, and 69.074° correspond to those of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. The peaks of $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ appear around $2\theta = 25.84^\circ$,

Figure 5. XRD of $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$.

34.065, 44.628, 54.582, and 64.061 and correspond to (211), (310), (410), (430), and (441), respectively. These results indicate that the synthesized material is composed of γ -Fe₂O₃.

Figure 6 shows NH₂-Fe₂O₃/CS with various quantities of added DETA. The visible peaks at (310), (410), (430), and (441) are consistent. The EDS instrument was equipped with SEM, and the results confirm that the samples are composed of the elements N, Fe, and C (Figure 6).

Figure 6. XRD of NH₂-Fe₂O₃/CS with varying DETA levels; the inset is the EDS result of NH₂-Fe₂O₃/CS.

3.4. Nitrogen Adsorption Analysis

Figure 7 shows the nitrogen adsorption-desorption isotherms of NH₂-Fe₂O₃ and NH₂-Fe₂O₃/CS composites. After the sample was degassed, the nitrogen adsorption started, and then the multipoint BET method was applied. The pore-size distribution was computed from the desorption isotherm by applying the Barrett-Joyner-Halenda (BJH) approach [18].

Figure 7. N₂ adsorption-desorption isotherm curve with varying quantities of DETA.

The remarkable hysteresis loops signify the presence of a mesoporous structure [19]. In Figure 7, all samples at the same temperature present typical Langmuir IV curves, indicating that the obtained composites are mesoporous materials.

The textural properties of NH₂-Fe₂O₃/CS with different DETA volumes are summarized in Table 1. The surface area reached a peak at 233.026 m²·g^{−1} when DETA = 0.5 mL. The porous composites

generally had BET surface areas in the range of 55.41–233.03 $\text{m}^2\cdot\text{g}^{-1}$, total pore volumes of 0.24–0.54 $\text{cm}^3\cdot\text{g}^{-1}$, and diameters of 3.83–17.56 nm.

Table 1. Pore Structural Parameters of Samples.

Volume of DETA (mL)	Surface Area ($\text{m}^2\cdot\text{g}^{-1}$)	Pore Diameter (nm)	Pore Volume ($\text{cm}^3\cdot\text{g}^{-1}$)
0.5	233.03	3.83	0.24
1	70.39	15.44	0.54
2	55.41	17.51	0.38
3	57.11	17.47	0.37
4	62.75	17.56	0.33
5	64.20	12.34	0.26

3.5. Adsorption in Ternary Systems

The $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ adsorption capacities were obtained for Cu(II), Cd(II), and Pb(II), and the results are exhibited in Figure 8. The adsorption capacities of $\text{NH}_2\text{-Fe}_2\text{O}_3$ for Cu(II), Cd(II), and Pb(II) was 18.40, 10.80, and 39.30 $\text{mg}\cdot\text{g}^{-1}$, while those of $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ for Cu(II), Cd(II), and Pb(II) was 18.23, 3.32, and 32.46 $\text{mg}\cdot\text{g}^{-1}$. The order in which the heavy metals were adsorbed by both $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ was $\text{Pb(II)} > \text{Cu(II)} > \text{Cd(II)}$, which is consistent with the order found by Zhang [13] ($\text{Pb(II)} > \text{Cd(II)}$). However, because methyl acrylate and Fe_2O_3 are costly, $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ are more suitable for practical application in industry. When DETA = 5 mL, the adsorption rate of Pb(II) by $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ reached 98.25% and 81.14%, respectively, while the adsorption rate of Cu(II) was 46.00% and 45.58%, and the adsorption rate of Cd(II) was 27.01% and 8.29%. When DETA = 0.5 mL, although the specific surface area of the material was as high as 233.026 $\text{m}^2\cdot\text{g}^{-1}$, the porosity was 0.24 $\text{cm}^3\cdot\text{g}^{-1}$, which may decrease the adsorption rate of heavy metals. The adsorption rate of Pb(II) by $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ was much higher than that of Cu(II) and Cd(II). The adsorption rate of heavy metals by $\text{NH}_2\text{-Fe}_2\text{O}_3$ increased with the increase in DETA volume, while the adsorption rate of heavy metals by $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ first decreased and then increased as the DETA volume increased.

Figure 8. Adsorption rates of Pb^{2+} by $\text{NH}_2\text{-Fe}_2\text{O}_3$ and its $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ composites are different with different DETA concentrations.

NaCl was chosen as an ionic medium to research the impact of other ions co-existing in solution on metal uptake. When NaCl was added to the system, a dramatic change in preferential adsorption was observed. In the condition of stable inner-sphere complexes, the outer sphere was susceptible to ionic strength [20]. As a result, the order of selective adsorption changed to $\text{Cd(II)} > \text{Cu(II)} > \text{Pb(II)}$, which is the opposite of the order in the NaCl-free system.

4. Conclusions

The magnetic adsorbents $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{CS}$ were synthesized by a simple method, and SEM, EDS, TEM, XRD, and BET results show that the material is uniformly dispersed with good crystallinity and well-defined porous particles. Scanning electron microscopy analysis confirmed that the sample was composed of the elements N, Fe, and C; the material was mesoporous, the specific surface area was $55.41\text{--}233.03\text{ m}^2\cdot\text{g}^{-1}$, the total pore volume was $0.24\text{--}0.54\text{ cm}^3\cdot\text{g}^{-1}$, and the diameter was $3.83\text{--}17.56\text{ nm}$. The adsorption properties of the porous composites in aqueous solution were studied. The results indicate that the adsorption rate of lead (II) was significantly higher than that of copper (II) and cadmium (II). When NaCl was added to the system, the adsorption sequence was opposite of that in the NaCl-free system.

In general, the outstanding performances of the developed composites in this study suggest that they are promising adsorbents for the treatment of heavy metals, and these findings are useful for the separation and recovery of heavy metals from wastewater.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2071-1050/11/19/5186/s1>.

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