Facile preparation of $\alpha$-Fe$_2$O$_3$ nanorods and the promotion in Cr(VI) adsorption

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Abstract. We present a simple and effective method for the fabrication of $\alpha$-Fe$_2$O$_3$ nanorods by a hydrothermal process. Field-emission scanning electron microscopy (SEM), X-ray diffraction (XRD) and N$_2$ adsorption-desorption are used to analyze the morphology, phase structure and surface area for the as-prepared $\alpha$-Fe$_2$O$_3$ nanorods, implying the fine dispersion of nanorods as well as the much increased surface area. The adsorption capacity of the material was evaluated by the adsorption of Cr(VI) in waste water, and the $\alpha$-Fe$_2$O$_3$ nanorods exhibits the enhanced performance compared with the normal-$\alpha$-Fe$_2$O$_3$ nanoparticles. The adsorption of Cr(VI) on $\alpha$-Fe$_2$O$_3$ nanorods fits the Langmuir adsorption model, and was controlled by the chemical process according to the high correlation to the pseudo-second-order model.

1. Introduction

Among heavy metals in the natural environment, chromium is one of the widely distributed pollutants in water and soil, existing in two common oxidation states, Cr(III) and Cr(VI) [1]. In general, Cr(III) occurs naturally, while the emitted Cr(VI) is commonly derived from industrial processes, such as electroplating, metal finishing, pigment manufacture, tannery facilities, and chromium mining. Cr(VI), existing in most aquatic environments as water soluble oxy-anions, HCrO$_4$- or CrO$_4^{2-}$, is highly toxic and environmentally harmful once introduced into the environment [2]. Therefore, the development of technologies to prevent further chromium discharge and remediate Cr(VI) contamination are of great importance.

Up to date, various multifunctional materials, such as biochar [3], inorganic nanoparticles [4], metals [5], and polymer [6] have been employed as absorbents for the rapid removal of metal ions. Among these materials, hematite ($\alpha$-Fe$_2$O$_3$) being one of the most stable, non-toxic, environment-friendly and corrosion-resistant metal oxide has been paid more and more attention in wastewater treatment [7]. Moreover, $\alpha$-Fe$_2$O$_3$ has many applications such as catalysis, gas sensors, magnetic materials, drug delivery, and light-induced water splitting [8-12]. In the past, some groups have prepared different morphologies and crystal structures of Fe$_2$O$_3$ through hydrothermal methods, where it is shown that the Cr(VI) adsorption capacity of $\alpha$-Fe$_2$O$_3$ is highly related with morphologies and exposed crystal facet [13]. On the basis of the surface adsorption theory, adsorption capacity to substances to a large degree depends on surface area and surface chemical properties of adsorbent, which is closely correlated with
preparation parameters. Furthermore, the adsorption behavior of Cr(VI) mainly occurs on the surface, and this means the surface micro-structure of α-Fe₂O₃ may significantly affect the adsorption capacity. However, it is still a challenge to investigate relationship between the adsorption properties, different morphology, micro-structures and preparation parameters of α-Fe₂O₃.

In the present work, uniform nanorod and microsphere α-Fe₂O₃ are successfully synthesized by a facile hydrothermal method. The adsorption ability of as-synthesized α-Fe₂O₃ toward Cr(VI) is examined, and possible adsorption mechanism is deduced.

2. Experimental

2.1. Synthesis of α-Fe₂O₃ nanorods

In a typical preparation procedure, hexahydrate ferric chloride (FeCl₃·6H₂O, 1.0836 g), ascorbic acid (C₆H₈O₆, 0.7045 g) and urea (CO(NH₂)₂, 0.6006 g) were dissolved in 70 ml DI water. The mixed solution was transferred to a Teflon autoclave (100 ml) and reacted at 160 ºC for 4 h. After cooling to the room temperature, the obtained slurry was washed by DI water and ethanol, dried at 70 ºC for 12 h, and calcined at 400 ºC for 4 h. The obtained Fe₂O₃ was denoted as α-Fe₂O₃-NR. To investigate the effect of morphology on the adsorption capacity of Fe₂O₃ materials, another Fe₂O₃ material was also prepared, in which ascorbic acid was removed from the precursors, while the others step was same with the synthesis of α-Fe₂O₃-ND. The obtained Fe₂O₃ material was denoted as Fe₂O₃-NP.

2.2. Characterization

The surface morphology of the as-prepared materials was observed by field-emission scanning electron microscope (FE-SEM, Neon40esb Zeiss). The Brunauer-Emmett-Teller (BET) surface area of the sample was determined by nitrogen adsorption at 77 K, carried out on Micromeritics ASAP 2020. X-ray diffraction (XRD) was carried out on a Bruker D8-Advanced X-ray instrument using Cu Kα radiation (λ = 1.5418 Å).

2.3. Adsorption of Cr(VI) ions

In the present study, K₂Cr₂O₇ was used as the source of Cr(VI) ions. Different concentrations of Cr(VI) ions were prepared and the pH value was adjusted to 3 by HCl. In a typical adsorption capacity measurement, the concentration of adsorbents was 1 g·L⁻¹, and the concentration of Cr(VI) ions was determined by a UV-vis spectrophotometer (JASCO V-670) at the characteristic absorption wavelength of Cr(VI) of 325 nm. The amount of metal ions adsorbed at adsorption time t (qₜ, mg·g⁻¹), the amount of metal ions adsorbed at equilibrium (qₑ, mg·g⁻¹), and the removal efficiency (E%) of Cr(VI) was calculated by the following equations:

\[ q_t = \frac{(C_0 - C_t)V}{m} \]  
\[ q_e = \frac{(C_0 - C_e)V}{m} \]  
\[ E(\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \]

where \( C_t \) (mg·L⁻¹) is the concentration of Cr(VI) at time \( t \), \( V \) is the volume of the solution (L), \( q_t \) and \( q_e \) (mg·g⁻¹) are the amounts of adsorbed Cr(VI) at time \( t \) and at equilibrium time, respectively, \( m \) is the mass of adsorbents (g), and \( C_0 \) and \( C_e \) (mg·L⁻¹) are the initial and final concentrations of Cr(VI), respectively.
3. Results and Discussions

3.1. Characterizations of \( \alpha \)-Fe\(_2\)O\(_3\) materials
The morphology of as-prepared Fe\(_2\)O\(_3\) materials is observed by SEM measurement. From Figure 1a and b, the typical morphology of Fe\(_2\)O\(_3\)-ND is uniform nanorods, with the length and width of 485 and 77 nm, respectively, while the morphology of Fe\(_2\)O\(_3\)-NP is sphere with rough surface, the diameter of which is 10~30 \( \mu\)m. The surface area of Fe\(_2\)O\(_3\) materials were investigated by \( N_2 \) adsorption-desorption isotherms, which are 50.3 and 12.9 m\(^2\)/g for Fe\(_2\)O\(_3\)-ND and Fe\(_2\)O\(_3\)-NP, respectively. The SEM images, combining with \( N_2 \) adsorption-desorption results, imply that the addition of ascorbic acid greatly benefits the formation of uniform morphology of Fe\(_2\)O\(_3\) nanoparticles and favors the enlargement of surface area. Figure 1c displays the XRD patterns of Fe\(_2\)O\(_3\)-ND and Fe\(_2\)O\(_3\)-NP. Both the Fe\(_2\)O\(_3\) materials are assigned to \( \alpha \)-Fe\(_2\)O\(_3\) (PDF#33-0664), and the diffraction peak s at 24.2°, 33.2°, 35.7°, 40.9°, 49.6°, 54.2°, 62.5° and 64.2° are assigned to (012), (104), (110), (113), (024), (116), (214) and (310) planes of \( \alpha \)-Fe\(_2\)O\(_3\), respectively. By comparison, the Fe\(_2\)O\(_3\)-ND exhibits the much stronger intensity, suggesting that the introduction of ascorbic acid greatly facilitates the crystallization of \( \alpha \)-Fe\(_2\)O\(_3\).

![Figure 1. SEM images of Fe\(_2\)O\(_3\)-ND (a) and Fe\(_2\)O\(_3\)-NP (b), and XRD patterns of Fe\(_2\)O\(_3\) samples (c) (insert: surface areas of Fe\(_2\)O\(_3\) samples).](image)

3.2. Cr(VI) adsorption properties of \( \alpha \)-Fe\(_2\)O\(_3\) samples
Owning the large surface area and the uniform morphology, the Fe\(_2\)O\(_3\)-ND sample is expected to exhibit excellent adsorption capacity, which were evaluated using the toxic Cr(VI) as the aimed pollutants. Figure 2a shows the adsorption isotherms of Cr(VI) on Fe\(_2\)O\(_3\)-ND and Fe\(_2\)O\(_3\)-NP samples, obtained with different initial concentrations of Cr(VI) ranging from 10 to 110 mg·L\(^{-1}\), which indicates that Fe\(_2\)O\(_3\)-ND exhibits the better adsorption capacity, with a maximum adsorption capacity of 28.3 mg·g\(^{-1}\), while the maximum adsorption capacity of Fe\(_2\)O\(_3\)-NP is 14.6 mg·g\(^{-1}\). Both the Langmuir and Freundlich isotherm models are used to analyze the adsorption data presented in Figure 2a, which are described by Equations (4) and (5), respectively:

\[
\frac{c_e}{q_e} = \frac{1}{K_Lq_m} + \frac{c_e}{q_m} \quad \text{(4)}
\]

\[
\log q_e = \log K_f + \frac{1}{n}\log C_e \quad \text{(5)}
\]

From Figure 2b and c, the Langmuir adsorption model is adopted to fit the equilibrium adsorption data better for both the Fe\(_2\)O\(_3\)-ND and Fe\(_2\)O\(_3\)-NP samples according to the higher correlation coefficients (R\(^2\)), which are 0.9729 and 0.9822 for Fe\(_2\)O\(_3\)-ND and Fe\(_2\)O\(_3\)-NP, respectively, while the value of R\(^2\) of Freundlich models for Fe\(_2\)O\(_3\)-ND and Fe\(_2\)O\(_3\)-NP are 0.9684 and 0.8899, respectively.

Figure 3a displays the adsorption rate curves of Fe\(_2\)O\(_3\)-ND and Fe\(_2\)O\(_3\)-NP samples for Cr(VI) ion with the concentrations of 10 and 30 mg·L\(^{-1}\). Fe\(_2\)O\(_3\)-ND exhibits the much more rapid adsorption to Cr(VI), and the excellent adsorption capacity is attributed to the increased surface area caused by the
uniform nanoscale morphology. Figure 3b shows a simple kinetics analysis of adsorption using the pseudo-second-order model, which is expressed as equation (6):

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2q_e^2}$$

(6)

where $k_2$ is the pseudo-second-order rate constant ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). The correlation coefficients $R^2$ show high correlation for the two initial Cr(VI) concentrations for the two as-prepared Fe$_2$O$_3$ materials, thus the Cr(VI) adsorption on the two samples are both controlled by the chemical process [14-16].

Figure 2. (a) Cr(VI) ion adsorption curves of Fe$_2$O$_3$-ND and Fe$_2$O$_3$-NP samples. (b) Linear Langmuir adsorption isotherm of Fe$_2$O$_3$-ND for Cr(VI) ion, insert: linear Freundlich adsorption isotherm of Fe$_2$O$_3$-ND for Cr(VI) ion. (c) Linear Langmuir adsorption isotherm of Fe$_2$O$_3$-NP for Cr(VI) ion, insert: linear Freundlich adsorption isotherm of Fe$_2$O$_3$-NP for Cr(VI) ion.

Figure 3. (a) Adsorption rate curves of Fe$_2$O$_3$-ND and Fe$_2$O$_3$-NP samples for Cr(VI) ion with the concentrations of 10 and 30 mg L$^{-1}$. (b) The pseudo-second-order kinetic model of Fe$_2$O$_3$-ND and Fe$_2$O$_3$-NP samples for Cr(VI) ion adsorption with the concentrations of 10 and 30 mg L$^{-1}$.

4. Conclusion
In the present study, a novel $\alpha$-Fe$_2$O$_3$ nanorods was fabricated by a one-step hydrothermal method, and the uniform morphology could be attributed to the introduction of ascorbic acid in the precursors during the preparation. The $\alpha$-Fe$_2$O$_3$ nanorods exhibited a rapid adsorption to Cr(VI), and the excellent performance was mainly attributed to the fine dispersion and the consequently increased surface area. The adsorption of Cr(VI) on $\alpha$-Fe$_2$O$_3$ nanorods fit the Langmuir adsorption model, and the kinetic
analysis confirmed that the adsorption could be described by pseudo-second-order model, meaning that the adsorption was controlled by the chemical process.

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