Gram-grade Cr (VI) adsorption on porous Fe@SiO$_2$ hierarchical microcapsules

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ABSTRACT

In this work, porous Fe@SiO$_2$ hierarchical microcapsules were fabricated by reducing α-Fe$_2$O$_3$@SiO$_2$ micro-spindles, which were prepared by using a two-step solution method. These Fe@SiO$_2$ microcapsules were then employed to remove Cr (VI) ion from water. On the basis of Langmuir isotherms model, the maximum Cr (VI) adsorption capacities were estimated to be ca. 1400 and 1300 mg g^{-1} at 305 and 310 K, respectively. These values, to our knowledge, were much higher than those in previous reports for many other Fe-based adsorbents. Besides, the initial Cr (VI) adsorption rate was calculated to be ca. 19 mg g^{-1} min^{-1} that was significantly higher than those reported in previous literatures, and hence improving the adsorptive efficiency of Fe@SiO$_2$ microcapsules in practical water treatment. Thermodynamic analyses of enthalpy, entropy and Gibbs free energy further evidenced that these outstanding kinetics and equilibrium results were mainly due to a physical adsorption process, accompanied by a chemisorption associated with the reduction of Cr (VI) to Cr (III). The gram-grade Cr (VI) adsorption capacities and easy magnetic separation are highly desirable for their widespread potential applications in water treatment.

1. Introduction

In recent years, the discharge of industrial, agricultural, domestic and municipal waste effluents into water bodies has inevitably resulted in an increased flux of toxic pollutants. Among water pollutants, metal ions (such as Pb (II), Cr (iv), As (III), Cu (II), Cd (III), Co (III), Co (II), Mn (II) and Hg (II)) have drawn serious concern because they are non-biodegradable and tend to accumulate in living organisms [1–3]. For example, Cr (VI) ions can cause serious diseases and disorders due to its strong oxidizability, high solubility, non-biodegradability and bioaccumulation. In aqueous solution, Cr (VI) exists in the form of chromate CrO$_4$$^{2-}$, dichromate Cr$_2O_7$$^{2-}$ and hydrogen chromate HCrO$_4$$^{2-}$. CrO$_4$$^{2-}$ is predominant in basic solutions, H$_2$CrO$_4$ is predominant at pH < 1 while HCrO$_4$$^{2-}$ and Cr$_2$O$_7$$^{2-}$ are predominant at pH 2–6 [4]. The maximum contaminant level of chromium in domestic water supplies has been set by World Health Organization (WHO) as 50 μg L^{-1} [5,6]. Therefore, it is imperative to seek for effective and economic technologies for Cr (VI) removal from waste water.

Until now, multiple technologies have been developed for water treatment, including adsorption, chemical precipitation, membrane processes, ion exchange, sedimentation, biological treatment, electro-dialysis, and reverse osmosis process [7–9]. Most of these techniques have limitations such as high cost, complicated treatment processes and high energy requirements, or they risk introducing secondary pollution [10]. Among these technologies, adsorption features the merits of its quite ease, low cost, high efficiency, and environmental benignity [11,12]. The selection of an ideal adsorbent plays an important role in water treatment. Traditional adsorbents (e.g., activated carbon, clay, and zeolite) are effective because of its high specific surface area (SSA), but they are difficult to be separated from water and hence may cause secondary pollution. Alternatively, magnetic nano-adsorbents also possess high SSA, but they have many drawbacks including long removal time and low removal efficiencies. In contrast, magnetic micro-sized hierarchical structures possess necessary mechanical strength that can sustain water flow sufficiently, and they can be easily separated from wastewater by a magnetic field. Besides, the nano-sized building blocks of the structures provide high SSA and high removal capacity for heavy metal ions.

Herein, porous Fe@SiO$_2$ hierarchical microcapsules were successfully synthesized for water treatment. In this structure, porous zero valent iron is used to remove Cr (VI) ions in pollutants [13–16]. Owing to its high reducibility, it was expected to show a higher chemical reduction rate for Cr (VI) ions [17,18]. Besides, mesoporous SiO$_2$ provides effective diffusion channels and active

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adsorption sites for Cr (VI) ions in waste water. It is anticipated that this structural design will shed some light on the development of robust magnetic adsorbents.

2. Experimental

2.1. Synthesis of porous Fe@SiO₂ hierarchical microcapsules

All chemicals were of analytical grade and used as received without further purification.

2.1.1. Synthesis of spindle-like α-Fe₂O₃

The synthetic route was reported elsewhere [19]. In a typical experiment procedure, 3 mL of aqueous FeCl₃·6H₂O solution (0.5 mol L⁻¹) and 3 mL of aqueous (NH₄)₂HPO₄ solution (0.05 mol L⁻¹) were mixed with vigorous stirring. De-ionized water was then added to a final volume of 40 mL. After stirring for 10 min, the mixture was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 70 mL for hydrothermal treatment at 220 °C for 3 h. After the autoclave had cooled down to room temperature naturally, the precipitate was separated by centrifugation, washed successively with distilled water and absolute ethanol, and dried in the air at 60 °C for 4 h (Scheme 1(a)).

2.1.2. Synthesis of spindle-like α-Fe₂O₃@SiO2

The as-obtained α-Fe₂O₃ product was dispersed into a solution, which contains 0.1 g of cetyltrimethylammonium bromide (CTAB), 60 mL of de-ionized water, and 60 mL of ethanol. Upon stirring, a solution containing 150 μL of tetraethoxysilane (TEOS), 2 mL of ammonia hydroxide and 20 mL of ethanol was added. After 6 h, the precipitate was centrifuged and washed with distilled water and absolute ethanol, and dried in the air at 60 °C for 4 h (Scheme 1(b)).

2.1.3. Synthesis of porous α-Fe₂O₃@SiO2

The above product was suspended in a 180 mL of aqueous solution containing 1.8 g of polyvinylpyrrolidone (PVP K-30, MW 10 000) and 11.34 g of oxalic acid. After maintaining at 60 °C for 10.5 h, α-Fe₂O₃ spindles were partially dissolved to yield numerous voids (Scheme 1(c)). The as-obtained powder was then calcined in the air at 600 °C for 6 h to totally remove CTAB (Scheme 1(d)).

2.1.4. Synthesis of porous Fe@SiO₂

The as-obtained powder was transferred to a tube furnace under the atmosphere of pure hydrogen (99.99%), and maintained at 525 °C for 4 h. The final product was washed with distilled water and absolute ethanol, and dried in the air at 60 °C for 4 h (Scheme 1(e)).

2.2. Characterization

XRD patterns were recorded on a powder X-ray diffractometer (Rigaku D/max-rA; Japan) equipped with a rotating anode and a Cu-K$_{\alpha 1}$ radiation source (λ = 1.5406 Å) at a step width of 0.02°. Scanning electron microscope (SEM) images were collected on a field-emission scanning electron microscope (JEOL JSM-6700F, Japan). Transmission-electron microscope (TEM) images were performed on the JEOL 2010 TEM (Japan) with an operating voltage of 200 kV. The high resolution transmission-electron microscope (HRTEM) experiments were conducted using a Field Emission Gun (FEG) JEOL 2010F microscope (Japan) with a point resolution of 0.19 nm. Fourier transform infrared (FTIR) spectrometry was performed on KBr disks of the powdered samples using a BRUKER TENSOR 27 FTIR spectrometer. The N₂ adsorption and desorption isotherm was conducted using a Quantachrome Instruments, NOVA 1000e. The iso-electric point (IEP) of the sample was measured by testing the zeta-potential in aqueous solution on a Zeatsizer Nano

ZS (Malvern Instruments). Surface charge density was determined by conduct metric titration method.

2.3. Adsorption measurements

Solutions with different Cr (VI) concentrations were prepared using K₂Cr₂O₇ as the source of heavy metal ions. For the adsorption kinetic study of Cr (VI), 40 mg as-prepared product was added into 60 mL Cr (VI) solution with initial Cr (VI) concentration of 25 mg L⁻¹ for different adsorbing time. To obtain the adsorption equilibrium isotherms, 20 mg as-synthesized product was added into a set of 30 mL Cr (VI) solutions with different Cr (VI) concentrations, and vigorously stirred for 12 h at three different temperatures (T = 305, 310 and 315 K). No pH buffers were used during the adsorption experiments and all the equilibrium pH values were measured between 4.84 and 5.83. After adsorption, the adsorbent was magnetically separated by a magnet from Cr (VI) solutions. Subsequently, Cr (VI) concentrations in supernatant were determined by inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin-Elmer, Optima 8000). To investigate the effect of pH value on Cr (VI) adsorption, pH values of solutions (Cr (VI), 100 mg L⁻¹) after the addition of adsorbents were adjusted to 3, 5, 7, 9 and 11 at room temperature by using 1 mol L⁻¹ HCl or NaOH solutions.

3. Result and discussion

3.1. Porous Fe@SiO₂ hierarchical structure

The chemical composition of initial precursor is shown in Fig. 1(a), in which all the diffraction peaks belong to α-Fe₂O₃ (JCPDS No: 33-0664). The morphology of α-Fe₂O₃ precursor resembles spindle, which is ca. 1.5 μm long and 0.2 μm wide (Fig. 1(b)). After coating with SiO₂, the morphology of the product is virtually unchanged, but these spindles severely agglomerate together (Fig. 1(c)). The coated SiO₂ layer is about 20 nm thick (inset of Fig. 1(c)). After etching treatment, α-Fe₂O₃@SiO₂ spindles are broken at either end (Fig. 1(d) and its inset). The morphology of final product is shown in Fig. 1(e), wherein almost all the spindles are open-ended. Upon closer scrutiny, the surface of these spindles is rough in texture or even scratched out from the middle (Fig. 1(f)). One can also clearly observe the porous characteristics from the TEM image in the inset of Fig. 1(f). The XRD pattern of the final product in Fig. 1(a) exhibits pronounced iron peaks (JCPDS No: 87-0721). However, the XRD peaks of amorphous SiO₂ are too inconspicuous to be observed. Given that the SiO₂ shell cannot be etched away during the whole synthetic route, the composition of final product is thus determined to be Fe@SiO₂. The Fe@SiO₂ product can rapidly response to an external magnetic field within 1 s (inset of Fig. 1(a)). The highly-magnified TEM image in Fig. 2(a) reveals the polycrystalline feature of iron cores, which can be strongly evidenced by the selected-area electron diffraction (SAED) pattern in the inset of Fig. 2(b). The HRTEM image of Fig. 2(b) shows the 2.03 Å fringe spacing, which corresponds to the (110) inter-planar spacing of iron.

To investigate the porous character of Fe@SiO₂ architectures, nitrogen adsorption-desorption isothermals were performed (Fig. 3). Fig. 3 shows the isothermals exhibit type IV characteristics according to the classification of the International Union of Pure and Applied Chemistry. The Brunauer-Emmett-Teller (BET) SSA is estimated to be 400.6 m² g⁻¹, which is mainly attributed to numerous mesopores in SiO₂ shells and micropores in iron cores. On the other hand, Barrett-Joyner-Halenda (BJH) desorption cumulative volume of pores is calculated to be ca. 0.29 cm³ g⁻¹ and the size of mesopores is averaged to be ca. 7.5 nm (inset of Fig. 3).