Facile preparation of magnetic mesoporous MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composites for Cr(VI) adsorption and reduction\textsuperscript{*}

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Abstract

Chromium-contaminated water is regarded as one of the biggest threats to human health. In this study, a novel magnetic mesoporous MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composite was prepared by a facile one-step modification method and applied to remove Cr(VI). X-ray diffraction, scanning electron microscopy, transmission electron microscopy, specific surface area, and vibrating sample magnetometer were used to characterize MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composites. The morphology analysis showed that the composites displayed a core-shell structure. The outer shell was mesoporous silica with CTAB and the core was MnFe\textsubscript{2}O\textsubscript{4} nanoparticles, which ensured the easy separation by an external magnetic field. The performance of MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composites in Cr(VI) removal was far better than that of bare MnFe\textsubscript{2}O\textsubscript{4} nanoparticles. There were two reasons for the effective removal of Cr(VI) by MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composites: (1) mesoporous silica shell with abundant CTA\textsuperscript{+} significantly enhanced the Cr(VI) adsorption capacity of the composites; (2) a portion of Cr(VI) was reduced to less toxic Cr(III) by MnFe\textsubscript{2}O\textsubscript{4}, followed by Cr(III) immobilized on MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composites, which had been demonstrated by X-ray photoelectron spectroscopy results. The adsorption of Cr(VI) onto MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB followed the Freundlich isotherm model and pseudo-second-order model. Tests on the regeneration and reuse of the composites were performed. The removal efficiency of Cr(VI) still retained 92.4\% in the sixth cycle. MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composites exhibited a great potential for the removal of Cr(VI) from water.

1. Introduction

Chromium is a common pollutant in environment, existing in two stable oxidation states, Cr(VI) and Cr(III). Cr(III) is less toxic, less soluble, and less transferred than Cr(VI). Cr(VI) can invade the human body by digestive tract, respiratory tract, skin, or mucous membrane, and accumulate in the body, and lead to pulmonary congestion and liver damage eventually. Even more serious is the fact that Cr(VI) has carcinogenicity and mutagenicity to living organism (Raji and Anirudhan, 1998). There are extensive anthropogenic sources of Cr(VI), such as electroplating, chemical manufacturing, mineral engineering, pigment wastes, and tanning process. Because of the high toxicity, a large number of methods have been developed to remove Cr(VI) ions from the wastewater, including adsorption (Liu et al., 2010), chemical reduction (Liu et al., 2010; Fu et al., 2015), biological process (He et al., 2015), and so on. As an effective and cost-efficient technique, adsorption has been one of the most popular techniques for Cr removal (Wang et al., 2015).

In recent years, the application of MnFe\textsubscript{2}O\textsubscript{4} nanoparticles in environmental remediation has attracted increasing attention. As is expected, MnFe\textsubscript{2}O\textsubscript{4} nanoparticles show great advantages in fine particle size, relatively high surface area, high catalytic performance, and high saturation magnetization (Rocher et al., 2008; Pereira et al., 2012). Compared with Fe\textsubscript{3}O\textsubscript{4}, γ-Fe\textsubscript{2}O\textsubscript{3}, CoFe\textsubscript{2}O\textsubscript{4}, and NiFe\textsubscript{2}O\textsubscript{4}, MnFe\textsubscript{2}O\textsubscript{4} has greater biocompatibility and magnetic susceptibility (Lee et al., 2006; Tromsdorf et al., 2007). The separation of MnFe\textsubscript{2}O\textsubscript{4} nanoparticles from aqueous solution can be achieved easily by an external magnetic field, providing a good method for practical operation. Previous studies showed that MnFe\textsubscript{2}O\textsubscript{4} materials can be used to remove heavy metals (Hu et al., 2007; Zhang et al., 2010) and organic pollutants (Nguyen et al., 2011; Liu et al., 2014). However, MnFe\textsubscript{2}O\textsubscript{4} nanoparticles tend to aggregate because of the small particle size and magnetism, leading to a decrease of surface area and durability, which would prevent the
materials from applying to practice (Liu et al., 2008).

To ease the aggregation of MnFe2O4 nanoparticles and improve their performance in contaminants removal, a general strategy is to incorporate MnFe2O4 nanoparticles into support materials. Various solid materials, such as activated carbon (Ai et al., 2010), graphene (Guo et al., 2014), silica (Sun et al., 2013), and TiO2 (Yao et al., 2015) are often used as support materials to improve the properties of raw materials. Nevertheless, some support materials have limitations for comprehensive application, such as complexity of synthesis procedures, high cost, and uneven loading (Liu et al., 2015). Mesoporous silica was considered to be one of the most ideal carriers due to its well-defined pore structures, chemical inertness, low cost, and facile functionalization (Yang et al., 2004). For example, Wang et al. (2010) reported that mesoporous silica material exhibited good performance for the removal of Hg2+. The above procedures were kept on for another 1 h at 75 °C until the pH arrived at 12.0. The reaction mixture was transferred to a stainless-steel autoclave with TeO2 (150 mL, 95%) containing NH4NO3 (0.3 g), and the mixture was stirred at 75 °C for 8 h. To investigate the role of CTAB in Cr(VI) removal, the extraction of CTAB in MnFe2O4@SiO2–CTAB composites was carried out. MnFe2O4@SiO2–CTAB composites (1.0 g) were dispersed in ethanol (150 mL, 95%) containing NH4NO3 (0.3 g), and the mixture was stirred at 60 °C for 15 min. Solids were separated by a magnet and washed with cold ethanol. The above procedures could be repeated twice. The final product was MnFe2O4@SiO2.

### 2.3. Cr(VI) removal experiments

0.28 g of MnFe2O4@SiO2–CTAB composites was added to 100 mL of synthetic Cr(VI) wastewater with the initial concentration of 20.0 mg/L and mixed by a thermostatic shaker. To study the impact of solution pH on Cr(VI) removal, the initial pH of the solution was adjusted to different pH values (3.0, 5.0, 7.0, and 9.0) with H2SO4 or NaOH. After removal experiments, MnFe2O4@SiO2–CTAB composites were separated by a permanent magnet and the supernatants were collected to measure the residual concentration of Cr(VI). The comparative experiments among MnFe2O4, MnFe2O4@SiO2, and MnFe2O4@SiO2–CTAB were performed as well. All experiments were conducted in triplicate at the room temperature of 25 °C, and average values along with one standard deviation were presented.

### 2.4. Adsorption isotherm

The adsorption isotherms studies were conducted by varying the initial concentration of Cr(VI) solution from 0 to 240 mg/L (0, 20, 40, 50, 80, 120, 180, 240 mg/L). A given amount of MnFe2O4@SiO2–CTAB (0.14 g) was added in 50 mL of Cr(VI) solution at initial pH 3.0. The mixture was continuously shaken at 130 rpm on a thermostatic shaker for 12 h under controlled temperature condition (25 °C). The kinetic experiments were carried out using the same method as described in Cr(VI) removal experiments. The equilibrium adsorption capacity (qe) (mg/g) for Cr(VI) was calculated according to the following equation:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

(1)

Where C0 and Ce (mg/L) are the initial and equilibrium Cr(VI) concentrations, respectively, V (L) is the volume of Cr(VI) solution, and m (g) is the mass of MnFe2O4@SiO2–CTAB composites.
2.5. Regeneration and reuse experiments

NaOH solution was used as eluent to desorb Cr(VI). After Cr(VI) removal experiment, the Cr loaded MnFe₂O₄@SiO₂–CTAB composites were separated by a magnet and then added in 50 mL 0.01 M NaOH solution. The mixture was shaken for 2 h. After that, the composites were collected by a permanent magnet and rinsed with deionized water. Then the composites were applied to remove Cr(VI) in the succeeding cycle. To investigate the reusability of the composites, experiments on regeneration and reuse were carried out in 6 consecutive cycles. The supernatants of the solutions (in regeneration and reuse experiments) were collected to measure the concentration of Cr(VI).

2.6. Analytical methods

2.6.1. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and transmission electron microscopy (TEM)

The morphology of MnFe₂O₄@SiO₂–CTAB was examined by an S-4800 SEM (Hitachi S-4800, Japan) equipped with an EDS and a JEM-2100 TEM (JEOL JEM-2100, Japan). Elemental mappings of MnFe₂O₄@SiO₂–CTAB after reaction were also performed.

2.6.2. X-ray diffraction (XRD), specific surface area, and vibrating sample magnetometer (VSM)

XRD analysis was obtained by an X-ray diffractometer (Bruker D8, Germany) using Cu Kα radiation. The specific surface area of MnFe₂O₄@SiO₂–CTAB was determined by Brunauer-Emmett-Teller (BET) N₂ adsorption analysis using a surface area analyzer (Nova, 2000ce; Quantachrome Instrument, USA). Magnetic properties were tested by a VSM (EV7, ADE, USA) at room temperature.

2.6.3. Fourier transformed infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS)

FT-IR (Nicolet 6700, Thermo fisher, USA) was used to analyze the molecular structure of MnFe₂O₄@SiO₂–CTAB before and after reaction. The XPS spectra of the composites before and after reaction were investigated by an Amicus XPS (Shimadzu Co., Japan) using normal Al Kα radiation (1486.8 eV) under a residual pressure of 2 × 10⁻¹⁰ Torr. Data analysis involved smoothing, non-linear Shirley-type background subtraction, and curve fitting using mixed Gaussian-Lorentzian functions. Spectral bands were deconvoluted into peaks with the software XPSPEAK from RCSMS lab using an integrated background subtraction.

2.6.4. Determination of Cr(VI) and Cr(III) concentrations

The amount of Cr(VI) in solution was determined with 1,5-diphenylcarbazide colorimetric method using a UV/visible spectrophotometer (UV2400, China) (λₘₐₓ = 540 nm) (Wang et al., 2015). The concentration of residual total chromium in solution was measured using a flame atomic absorption spectrometer (AAS, Z-20000, Hitachi, Japan). The difference between total chromium and Cr(VI) was calculated as the concentration of Cr(III).

3. Results and discussion

3.1. Characterization of MnFe₂O₄ and MnFe₂O₄@SiO₂–CTAB

Fig. 1 shows the XRD patterns of (a) MnFe₂O₄ and (b) MnFe₂O₄@SiO₂–CTAB. The diffraction peaks of MnFe₂O₄ fit perfectly with the standard data of the spinel MnFe₂O₄ (JCPDS Card no. 74-2403). Typical crystal faces like (111), (220), (311), (222), (400), (422), (511), and (440) can be identified from the corresponding diffraction peaks of MnFe₂O₄, which are consistent with the results reported by previous research (Bao et al., 2013). These narrow sharp peaks demonstrated that MnFe₂O₄ particles were highly crystallized. The diffraction peaks of MnFe₂O₄@SiO₂–CTAB composites (Fig. 1(b)) were similar to those of MnFe₂O₄ nanoparticles (Fig. 1(a)), indicating that MnFe₂O₄ nanoparticles were well retained in the modification process. MnFe₂O₄@SiO₂–CTAB composites exhibited a broad peak at around 2θ = 22°, which could be assigned to the mesoporous silica layer (Liu et al., 2014).

According to the SEM image of MnFe₂O₄ (Fig. 2(a)), the primary particle sizes ranged from 100 nm to 150 nm. After modification, the final composites were spherical shapes and the diameter of the composites increased to 400–800 nm (Fig. 2(b)). As observed in TEM images (Fig. 2(c) and (d)), MnFe₂O₄@SiO₂–CTAB composites displayed a typical core-shell structure. The outer shell was mesoporous silica with CTAB, while the core was MnFe₂O₄ nanoparticles. The thickness of mesoporous silica layer was about 100–150 nm. The silica layer can protect MnFe₂O₄ nanoparticles from corrosion and maintain the magnetism of MnFe₂O₄, which was favorable to separate MnFe₂O₄@SiO₂–CTAB composites from water.

The nitrogen adsorption/desorption isotherms and pore-size distribution of MnFe₂O₄@SiO₂–CTAB composites are displayed in Fig. 3. According to the nomenclature of the International Union of Pure and Applied Chemistry (IUPAC), the curve can be classified as a type-IV isotherm which was characterized by the appearance of hysteresis loops within relative pressure (P/P₀) of 0.4–1.0, indicating that the silica shell was mesoporous (Rahman et al., 2013; Liu et al., 2014). A wide hysteresis area of nitrogen adsorption/desorption isotherms could be observed, which implied that the pores distributed widely (Fang et al., 2015), as shown in the Inset of Fig. 3. Since the interaction between silica and CTAB was complex, MnFe₂O₄@SiO₂–CTAB composites had a few systems of pores centered at 2.49, 3.92, 5.07, and 5.74 nm. This also proved that MnFe₂O₄@SiO₂–CTAB composites were mesoporous materials. The specific surface area of MnFe₂O₄@SiO₂–CTAB composites was 53.4 m²/g.

In order to study magnetic properties of the samples, magnetic hysteresis measurements were performed in an applied magnetic field at room temperature. Fig. 4 displays the magnetic hysteresis loops of MnFe₂O₄, MnFe₂O₄@SiO₂, and MnFe₂O₄@SiO₂–CTAB. The Inset is the magnified views of the hysteresis loops at low applied fields. These hysteresis loops were typical for a soft magnetic material as shown by their long and narrow hysteresis loops, minor
Fig. 2. The SEM images of (a) MnFe$_2$O$_4$ and (b) MnFe$_2$O$_4$@SiO$_2$–CTAB, and the TEM images ((c) and (d)) of MnFe$_2$O$_4$@SiO$_2$–CTAB.

Fig. 3. Nitrogen adsorption/desorption isotherms of MnFe$_2$O$_4$@SiO$_2$–CTAB. Inset: Pore-size distribution of MnFe$_2$O$_4$@SiO$_2$–CTAB.

Fig. 4. Room-temperature magnetization curves of MnFe$_2$O$_4$, MnFe$_2$O$_4$@SiO$_2$, and MnFe$_2$O$_4$@SiO$_2$–CTAB. Inset: Magnified views of the hysteresis loops at low applied fields.
coercivity (Hc), minor remanent magnetization (Mr) and minor hysteresis losses. The saturation magnetization (Ms) values were measured to be 37.1, 20.5, and 18.4 emu/g for MnFe2O4, MnFe2O4@SiO2, and MnFe2O4@SiO2–CTAB, respectively. Since mesoporous silica and CTAB coated on MnFe2O4 nanoparticles after modification, the saturation magnetization decreased to 18.4 emu/g, and this value was still large enough to separate the composites easily by an external magnetic field. The digital images in Fig. 4 show the separation of MnFe2O4@SiO2–CTAB composites from aqueous dispersion using a magnet.

3.2. Cr(VI) removal by MnFe2O4@SiO2–CTAB

3.2.1. Effect of initial pH on Cr(VI) removal

The performance of MnFe2O4@SiO2–CTAB composites strongly depended on the solution pH. As shown in Fig. 5, the removal efficiency of Cr(VI) decreased sharply with the increase of pH value. At pH 3.0, more than 99% of Cr(VI) in the solution can be removed after reaction. However, at pH 9.0, the removal efficiency of Cr(VI) was only 12.1% after reaction. The oxocations of Cr(VI) are known to exist as described in the following equations (Eqs. (2)–(5)) (Xu et al., 2015).

\[
\begin{align*}
\text{H}_2\text{CrO}_4 & \rightarrow \text{HCrO}_4^- + \text{H}^+ , \quad K_1 = 1.21 \\
\text{Cr}_2\text{O}_7^{2-} & \rightarrow 2\text{HCrO}_4^- , \quad K_2 = 35.5 \\
\text{HCrO}_4^- & \rightarrow \text{CrO}_4^{2-} + \text{H}^+ , \quad K_3 = 3 \times 10^{-7} \\
\text{HCrO}_7^- & \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}^+ , \quad K_4 = 0.85
\end{align*}
\]

At pH 3.0, the monovalent HCrO4 was the dominant species, while the HCrO4 converted to the divalent CrO4^2− with the increase of pH value (Dinda and Saha, 2015). At low pH, the removal of Cr(VI) was through the adsorption of HCrO4 by MnFe2O4@SiO2–CTAB composites, but at high pH, the removal of Cr(VI) was mainly due to the adsorption of CrO4^2−. There were a large number of CTA− cations existing on the MnFe2O4@SiO2–CTAB composites. The HCrO4 combined with CTA− cations (C_{16}H_{33}(CH_{3})_{3}N^−) and formed ion-pairs, but the divalent CrO4^2− (dominant at pH > 6.8) could not form ion-pairs with CTA^− cations (Venkateswaran and Palanivelu, 2004). These reasons explained the high Cr(VI) uptake at pH 3.0. As the pH increased, the concentration of hydroxyls in the mixed solution increased. The hydroxyls competed with Cr(VI) anions for the adsorption sites on MnFe2O4@SiO2–CTAB phase, finally causing a decrease in removal efficiency of Cr(VI). Based on the results of effect of initial pH on Cr(VI) removal, the following Cr(VI) removal experiments were performed at the pH of 3.0 unless otherwise specified.

The changes of pH during the reaction process were also investigated (Inset of Fig. 5). The pH of the solution increased in acidic conditions and decreased in alkaline conditions, such as, from 3.0 to 3.9, 5.0 to 6.7, and 9.0 to 7.5, respectively. To further evaluate the pH changes in Cr(VI) removal by MnFe2O4@SiO2–CTAB, contrast experiments on the effect of initial pH on the sorbate of Cr(VI) and adsorbent of MnFe2O4@SiO2–CTAB were performed separately (Fig. 1S) and discussed in Supplementary Material.

3.2.2. Comparative experiments among MnFe2O4, MnFe2O4@SiO2, and MnFe2O4@SiO2–CTAB

Comparative experiments of Cr(VI) removal among MnFe2O4, MnFe2O4@SiO2, and MnFe2O4@SiO2–CTAB were conducted. From Fig. 6, it can be seen that the performance of MnFe2O4@SiO2–CTAB composites in Cr(VI) removal was far better than that of MnFe2O4 and MnFe2O4@SiO2. The fast and effective Cr(VI) removal was attributed to a higher association rate between Cr(VI) and MnFe2O4@SiO2–CTAB composites, which implied that mesoporous silica shell with abundant CTA− enhanced the Cr(VI) adsorption capacity of the composites. The Cr(VI) ions were removed rapidly by MnFe2O4@SiO2–CTAB composites in 30 min, since there were lots of active sites at first stage. As the reaction time prolonged, the concentration of Cr(VI) in the mixed solution and active sites on MnFe2O4@SiO2–CTAB composites gradually reduced due to the accumulation of Cr species on the composites.

3.3. Adsorption isotherm and adsorption kinetics

3.3.1. Adsorption isotherms

For better understanding the Cr(VI) adsorption characteristics on MnFe2O4@SiO2–CTAB, two well-known adsorption isotherm
adsorption intensity, respectively. The Freundlich constants and represent adsorption capacity and equations were employed in the study (Wang et al., 2015).

\[
q_e = \frac{q_{\text{max}} k_e C_0}{1 + K_e C_0}
\]

(6)

\[
q_e = K_F C_0^{1/n}
\]

(7)

Where \(q_e\) and \(q_{\text{max}}\) are the amount of Cr(VI) adsorbed at equilibrium and the maximum adsorption capacity (mg/g), respectively; \(K_e\) is a Langmuir constant related to the affinity of the binding sites and energy of adsorption (L/mg). \(K_F\) and \(n\) are Freundlich constants and represent adsorption capacity and adsorption intensity, respectively.

The adsorption isotherms of Cr(VI) on MnFe2O4@SiO2–CTAB are shown in Fig. 7, and the related model parameters are presented in Table 1. The maximum adsorption capacity \(q_{\text{m}}\) of MnFe2O4@SiO2–CTAB is 25.044 mg/g. The higher correlation coefficients \(R^2 = 0.994\) of Freundlich model indicated that the adsorption of Cr(VI) onto MnFe2O4@SiO2–CTAB is compliance with the Freundlich isotherm model. Besides, the value of \(n\) is in the range of 1–10, which indicates a favorable adsorption process (Gulnaz et al., 2004). The Freundlich isotherm is primarily based on an empirical equation to describe heterogeneous systems while the Langmuir adsorption isotherm assumes a homogeneous adsorption process (Wang et al., 2015).

### 3.3.2. Adsorption kinetics

In order to study the Cr(VI) removal by MnFe2O4@SiO2–CTAB composites, pseudo-first-order and pseudo-second-order kinetic models were used. The linear forms of the pseudo-first-order and pseudo-second-order models are shown in Eq. (8) and Eq. (9) (Molina et al., 2014), respectively.

\[
\frac{1}{q_e} = \frac{k_1}{q_{\text{e,exp}}} + \frac{1}{q_{\text{e,cal}}}
\]

(8)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_{\text{e,cal}}} + \frac{t}{q_{\text{e,cal}}}
\]

(9)

Where \(q_t\) and \(q_{\text{e,exp}}\) are the amounts of Cr(VI) adsorbed on MnFe2O4@SiO2–CTAB at time \(t\) and equilibrium, respectively; \(k_1\) and \(k_2\) are the kinetic rate constants of pseudo-first-order and pseudo-second-order reaction kinetics, respectively.

Fig. 2S is the plot of the pseudo-first-order kinetic model and pseudo-second-order kinetic model. The kinetics parameters were calculated and listed in Table 1. From Table 1, the pseudo-second-order model can better fit the experimental data with high \(R^2 (0.997–0.999)\), indicating that Cr(VI) adsorption on MnFe2O4@SiO2–CTAB, MnFe2O4@SiO2, and MnFe2O4 followed the pseudo-second-order model. Therefore, it may be concluded that chemisorption is the rate-controlling step of the adsorption process of Cr(VI) in this study.

### 3.4. Characterization of MnFe2O4@SiO2–CTAB after reaction with Cr(VI)

#### 3.4.1. EDS and SEM mapping

As shown in Fig. 8, the EDS spectra and SEM mappings indicated that the main elements of the composites after reaction were Mn, Fe, O, N, C, Si, and Cr. The new occurring Cr element indicated that the Cr(VI) in solution had transferred to the MnFe2O4@SiO2–CTAB composites phase. For the individual elemental mapping, the Mn, Fe, Si, and O elements showed similar mapping, demonstrating once again that MnFe2O4 nanoparticles were modified by mesoporous silica. Cr mapping was closely associated with Mn, Fe, Si, and O mappings, which implied that Cr species were immobilized on MnFe2O4@SiO2–CTAB composites after reaction.

#### 3.4.2. FT-IR analysis

The FT-IR spectra of MnFe2O4@SiO2–CTAB and Cr loaded MnFe2O4@SiO2–CTAB are shown in Fig. 9. MnFe2O4@SiO2–CTAB

![Fig. 7. Fitted adsorption isotherms of Cr(VI) on MnFe2O4@SiO2–CTAB.](image)

<table>
<thead>
<tr>
<th>Adsorbents</th>
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<td></td>
<td>(q_{\text{exp}}) (mg/g)</td>
<td>(k_1) (1/min)</td>
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<td>MnFe2O4@SiO2–CTAB</td>
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</table>
showed absorption bands at 1080 and 462 cm$^{-1}$, which were assigned to the vibration modes of Si–O–Si and Si–O, respectively (Ding et al., 2012; Mohapatra et al., 2015). Another band at 962 cm$^{-1}$ corresponded to the Si–OH bending vibration (Hakami et al., 2012), which shifted to 953 cm$^{-1}$ after reaction. The absorption band at 571 cm$^{-1}$ was ascribed to Mn–O stretching vibration (Pereira et al., 2012; Bao et al., 2013). The characteristic band near 1635 cm$^{-1}$ was derived from CTA$^+$ (Kong et al., 2014), which shifted to 1630 cm$^{-1}$ after reaction because CTA$^+$ combined with Cr(VI). Other bands at 1488, 2852, and 2923 cm$^{-1}$ were attributed to bending, symmetric, and asymmetric stretching vibration of –CH$_2$– of cetyltrimethylammonium, respectively (Ding et al., 2012; Araghi et al., 2015). The broad absorption peak at 3423 cm$^{-1}$ belonged to O–H stretching vibration, suggesting the existence of hydroxyl groups on the composites or this band can be assigned to the adsorbed water molecules (Hakami et al., 2012). As shown in curve (b) of Fig. 9, after reaction, a new absorption peak at 900 cm$^{-1}$ was observed, which belonged to Cr species (Xu et al., 2010). A few peaks shifted after reaction, which mainly involved in the interactions between the functional groups of

Fig. 8. The EDS spectra of (a) MnFe$_2$O$_4$@SiO$_2$–CTAB and (b) Cr loaded MnFe$_2$O$_4$@SiO$_2$–CTAB, SEM mapping of (c) Mn, (d) Fe, (e) Cr, (f) Si, (g) O, and (h) C in MnFe$_2$O$_4$@SiO$_2$–CTAB after reaction.
3.4.3. XPS analysis

Fig. 10 shows the XPS patterns of Cr 2p\textsubscript{3/2}, Mn 2p\textsubscript{3/2}, and O 1s of MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB before and after reaction. Cr XPS peak appeared after reaction (Fig. 10(a)). Cr 2p\textsubscript{3/2} peak was deconvoluted into two peaks, 66.4% of Cr(III) at 577.1 eV and 33.6% of Cr(VI) at 579.1 eV (Zapata et al., 2013; Dinda and Saha, 2015; Ying et al., 2015). This implied that both Cr(VI) and Cr(III) were synchronously existing on MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composites after reaction. Moreover, the Cr 2p\textsubscript{3/2} peak at 577.1 eV indicated the formation of Cr(OH)\textsubscript{3} in the process of reaction (Fu et al., 2015). The presence of Cr(VI) was attributed to the adsorption of Cr(VI) by MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composites. However, the existence of Cr(III) suggested that the Cr(VI) removal process involved the reduction transformation of Cr(VI) to Cr(III). As is known, Cr(III) forms different Cr(OH)\textsubscript{x} species in the pH range from 3.8 to 11.5 (Deshpande et al., 2005). The pH of solution increased from 3.0 to 3.9 during the Cr(VI) removal process (Inset of Fig. 5). Hence, the generated Cr(III) can be immobilized in the formation of Cr(OH)\textsubscript{3} precipitates on MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composites.

Moreover, the Cr 2p\textsubscript{3/2} peak at 577.1 eV indicated the formation of Cr(OH)\textsubscript{3} in the process of reaction (Fig. 10(a)). Cr XPS peak appeared after reaction (Fig. 10(a)). Cr 2p\textsubscript{3/2} peak was deconvoluted into two peaks, 66.4% of Cr(III) at 577.1 eV and 33.6% of Cr(VI) at 579.1 eV (Zapata et al., 2013; Dinda and Saha, 2015; Ying et al., 2015). This implied that both Cr(VI) and Cr(III) were synchronously existing on MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composites after reaction. Moreover, the Cr 2p\textsubscript{3/2} peak at 577.1 eV indicated the formation of Cr(OH)\textsubscript{3} in the process of reaction (Fu et al., 2015). The presence of Cr(VI) was attributed to the adsorption of Cr(VI) by MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composites. However, the existence of Cr(III) suggested that the Cr(VI) removal process involved the reduction transformation of Cr(VI) to Cr(III). As is known, Cr(III) forms different Cr(OH)\textsubscript{x} species in the pH range from 3.8 to 11.5 (Deshpande et al., 2005). The pH of solution increased from 3.0 to 3.9 during the Cr(VI) removal process (Inset of Fig. 5). Hence, the generated Cr(III) can be immobilized in the formation of Cr(OH)\textsubscript{3} precipitates on MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB composites.

As shown in Fig. 10(b), the XPS spectra of Mn 2p\textsubscript{3/2} can be fitted by two peaks at binding energies of 639.8 and 642.0 eV, which were assigned to the Mn(II) and Mn(III), respectively (Yao et al., 2014; Ren et al., 2015). According to the peak area analysis, after reaction with Cr(VI), the relative contents of Mn(II) reduced from 86.2% to 24.9%, and the relative contents of Mn(III) increased from 13.8% to 75.1%, implying the oxidation of Mn(II) to Mn(III) by Cr(VI). These results indicated that Mn(II) species on the surface of MnFe\textsubscript{2}O\textsubscript{4} could act as reductants to transfer Cr(VI) into Cr(III). The reduction property of MnFe\textsubscript{2}O\textsubscript{4} was also reported by previous research (Hu et al., 2007). With the reduction of Cr(VI), the H\textsuperscript{+} ions in mixing solution were consumed, which caused an ascendant of pH value in acidic reaction condition (Inset of Fig. 5).

Fig. 9. FT-IR spectra of (a) MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB and (b) Cr loaded MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB.

Fig. 10. XPS patterns of (a) Cr 2p\textsubscript{3/2}, (b) Mn 2p\textsubscript{3/2}, and (c) O 1s of MnFe\textsubscript{2}O\textsubscript{4}@SiO\textsubscript{2}–CTAB before and after reaction.
In XPS spectra of O 1s (Fig. 10(c)), the binding energies at 532.4, 531.4, and 529.9 eV represented Si–O, surface hydroxyl groups (–OH), and the surface lattice oxygen of metal oxides (O^{2−}), respectively (Yao et al., 2014; Fu et al., 2015; Ren et al., 2015). The hydroxyl groups derived from Si–OH groups, MnFe₂O₄ surface (Yao et al., 2014), and the adsorbed water molecules on MnFe₂O₄–SiO₂–CTAB composites. The presence of hydroxyl groups was favorable to the immobilization of Cr(III) via surface complexation (Xu et al., 2008; Tian et al., 2016) and precipitation. Besides, the AAS and UV/vis results showed that the amount of Cr(III) was almost negligible (<0.06 mg/L) in the final solution (Fig. 3S). The results demonstrated that MnFe₂O₄@SiO₂–CTAB composites exhibited a great potential for effective removal of Cr(VI) from aqueous solution.

3.5. Removal mechanism of Cr(VI)

Based on the above discussion, the facile one-step modification route and the removal mechanism of Cr(VI) were illustrated in Scheme 1. The Cr(VI) removal occurred due to two aspects. First, mesoporous MnFe₂O₄@SiO₂–CTAB composites with abundant CTA⁺ could adsorb Cr(VI) from aqueous solution effectively and rapidly as the HCrO₄⁻ (dominant at pH 3.0) anions can combine CTA⁺ cations and form ion-pairs (Eq. (10)). Second, Cr(VI) was reduced to less toxic Cr(III) with the assistance of H⁺ when Cr(VI) contacted with the surface of MnFe₂O₄. The electrons transferred from Mn(II) species of MnFe₂O₄ to Cr(VI). It should be pointed out that the reduction of Cr(VI) was most likely to occur in acidic condition. Relevant mechanism is shown in Eq. (11). However, few Cr(VI) ions were removed by MnFe₂O₄@SiO₂–CTAB composites in alkaline medium as shown in Eq. (12). The generated Cr(III) was immobilized via surface complexation and precipitation.

\[
\text{C}_{16}\text{H}_{33}(\text{CH}_3)\text{3N}^+ + \text{HCrO}_4^- \rightarrow \text{C}_{16}\text{H}_{33}(\text{CH}_3)\text{3N}^+ \cdots \text{HCrO}_4^- \quad (10)
\]

\[
\equiv 3\left(\text{Mn}^{2+} - \text{OH}^-\right) + \text{HCrO}_4^- + 7\text{H}^+ \rightarrow \equiv 3\left(\text{Mn}^{3+} - \text{OH}^-\right) + \text{Cr}^{3+} + 4\text{H}_2\text{O} \quad (11)
\]

\[
\equiv 3\left(\text{Mn}^{2+} - \text{OH}^-\right) + \text{CrO}_2^- + 4\text{H}_2\text{O} \rightarrow \equiv 3\left(\text{Mn}^{3+} - \text{OH}^-\right) + \text{Cr(OH)}_3^- + 5\text{OH}^- \quad (12)
\]

3.6. Regeneration and reuse of MnFe₂O₄@SiO₂–CTAB

The sustainability of water-treatment agent is quite important. An economic and sustainable chemical agent can be achieved through regeneration to restore the available sites and components present in the agent phase. To test the recycle property of MnFe₂O₄@SiO₂–CTAB composites, NaOH solution (0.01 M) were used as eluent. As shown in Fig. 11, the removal efficiency of Cr(VI) still retained 92.4% at the end of sixth cycle. The follows may be the reasons for the phenomenon. First, the desorption of Cr(VI) could regenerate the adsorption sites of MnFe₂O₄@SiO₂–CTAB composites, and the desorption can proceed according to Eq. (13) (Venkateswaran and Palanivelu, 2004). Second, Cr(III), the reduction product, did not occupy the adsorption sites of CTA⁺ on the sorbent because Cr(III) can not form ion-pair with CTA⁺ cations. The desorption efficiency of Cr(VI) in each cycle was shown in Fig. 11. The amount of desorbed Cr(VI) increased with the increasing of recycling times of the composites, indicating that less and less Cr(VI) was reduced to Cr(III) in the late-stage removal cycles due to the consumption of available reducing sites on the surface of MnFe₂O₄.

\[
\text{C}_{16}\text{H}_{33}(\text{CH}_3)\text{3N}^+ + \text{HCrO}_4^- + \text{OH}^- \rightarrow \text{C}_{16}\text{H}_{33}(\text{CH}_3)\text{3N}^+ + \text{CrO}_4^{2-} + \text{H}_2\text{O} \quad (13)
\]

4. Conclusions

Magnetic mesoporous composites (MnFe₂O₄@SiO₂–CTAB) with novel core-shell structure were first prepared, characterized, and applied to remove Cr(VI). MnFe₂O₄@SiO₂–CTAB composites were prepared by a facile one-step modification method. MnFe₂O₄ (served as the core of the composites) possessed interesting magnetic property and thus ensured the easy separation by an external magnetic field. The outer shell of the composites was mesoporous silica with CTAB. MnFe₂O₄@SiO₂–CTAB composites showed great performance in Cr(VI) removal, which was due to the adsorption of Cr(VI) on mesoporous silica shell with abundant CTA⁺ and reduction of Cr(VI) to less toxic Cr(III) by MnFe₂O₄ nanoparticles. The generated Cr(III) was immobilized by surface complexation and precipitation. The amount of Cr(III) was almost negligible in the final solution. Freundlich isotherm model yields a much better fit than that of Langmuir isotherm model in describing Cr(VI) adsorption. The adsorption process fits the pseudo-second-order kinetic model very well. The results of regeneration and reuse experiments proved that MnFe₂O₄@SiO₂–CTAB composites were
recyclable materials. From the above, the prepared MnFe2O4@SiO2–CTAB composites have a great potential as novel and efficient materials for the treatment of Cr(VI)-contaminated water.

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Appendix A. Supplementary data

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References


