



Invited paper

Facile preparation of magnetic mesoporous $\text{MnFe}_2\text{O}_4@/\text{SiO}_2$ –CTAB composites for Cr(VI) adsorption and reduction^{*}Na Li, Fenglian Fu^{*}, Jianwei Lu, Zecong Ding, Bing Tang, Jiabin Pang

School of Environmental Science and Engineering and Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China

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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 $\text{MnFe}_2\text{O}_4@/\text{SiO}_2$ –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 $\text{MnFe}_2\text{O}_4@/\text{SiO}_2$ –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_2O_4 nanoparticles, which ensured the easy separation by an external magnetic field. The performance of $\text{MnFe}_2\text{O}_4@/\text{SiO}_2$ –CTAB composites in Cr(VI) removal was far better than that of bare MnFe_2O_4 nanoparticles. There were two reasons for the effective removal of Cr(VI) by $\text{MnFe}_2\text{O}_4@/\text{SiO}_2$ –CTAB composites: (1) mesoporous silica shell with abundant CTA^+ 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_2O_4 , followed by Cr(III) immobilized on $\text{MnFe}_2\text{O}_4@/\text{SiO}_2$ –CTAB composites, which had been demonstrated by X-ray photoelectron spectroscopy results. The adsorption of Cr(VI) onto $\text{MnFe}_2\text{O}_4@/\text{SiO}_2$ –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. $\text{MnFe}_2\text{O}_4@/\text{SiO}_2$ –CTAB composites exhibited a great potential for the removal of Cr(VI) from water.

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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_2O_4 nanoparticles in environmental remediation has attracted increasing attention. As is expected, MnFe_2O_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_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, CoFe_2O_4 , and NiFe_2O_4 , MnFe_2O_4 has greater biocompatibility and magnetic susceptibility (Lee et al., 2006; Tromsdorf et al., 2007). The separation of MnFe_2O_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_2O_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_2O_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

^{*} This paper has been recommended for acceptance by Baoshan Xing.

^{*} Corresponding author.

E-mail address: fufenglian2006@163.com (F. Fu).

materials from applying to practice (Liu et al., 2008).

To ease the aggregation of MnFe_2O_4 nanoparticles and improve their performance in contaminants removal, a general strategy is to incorporate MnFe_2O_4 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 TiO_2 (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 Hg^{2+} from aqueous solution. Tsai et al. (2016) reported that carboxyl functionalized mesoporous silica was effective in the removal of cationic dyes. These studies revealed that mesoporous silica could potentially provide a favorable carrier for MnFe_2O_4 nanoparticles.

In this paper, a novel $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -CTAB composite was prepared by a facile one-step modification method, which has not been reported to date to the best of our knowledge. In $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -CTAB composites, mesoporous silica with CTAB was employed as the shell, while MnFe_2O_4 was as the core. Cetyltrimethylammonium bromide (CTAB) was a common cationic surfactant (the dissociated cetyltrimethylammonium (CTA^+) maintained the properties of surfactant), which was suitable for dispersing and pore-making (Wang et al., 2012). There was no need to remove the CTAB used as a pore-formed template of silica, because CTA^+ can combine Cr(VI) anions and form ion-pairs, which would facilitate the removal of Cr(VI) (Venkateswaran and Palanivelu, 2004). The performance of $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -CTAB composites in Cr(VI) removal was tested by batch experiments. Characterization of $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -CTAB composites before and after reaction with Cr(VI) was investigated to explore the reaction mechanism. Tests on the regeneration and reuse of the composites were performed. $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -CTAB composites revealed a great potential for the removal of Cr(VI) from water.

2. Experimental

2.1. Materials and reagents

Manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), and tetraethyl orthosilicate (TEOS) were purchased from Aladdin Industrial Corporation (Shanghai, China). Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and cetyltrimethylammonium bromide (CTAB, $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$) were obtained from Kelong Chemical Company (Chengdu, China). $\text{K}_2\text{Cr}_2\text{O}_7$ was used to prepare synthetic Cr(VI) wastewater. All chemicals were of analytical reagent grade and used without further purification. Deionized water was used throughout the experiments.

2.2. Synthesis of MnFe_2O_4 and $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -CTAB

2.2.1. Synthesis of MnFe_2O_4 nanoparticles

MnFe_2O_4 nanoparticles were synthesized by the hydrothermal method. 5.40 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.98 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 30 mL deionized water. NaOH solution (1.0 M) was added dropwise to the solution with simultaneous agitation at the reaction temperature of 75°C until the pH arrived at 12.0. The reaction was kept on for another 1 h at 75°C . The above procedures were conducted under a gentle N_2 gas stream of 2.5 L/min. Then the mixture was transferred to a stainless-steel autoclave with Teflon lining. After heating at 200°C for 5 h, the solid products were

rapidly collected by a magnet and repeatedly rinsed with deionized water. Following this, the products were dried at 60°C for 8 h. The color of MnFe_2O_4 nanoparticles was black.

2.2.2. Synthesis of $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -CTAB composites

$\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -CTAB composites were prepared by a facile one-step modification route adapted from the method of Wang et al. (2010) and classical Stöber. First, MnFe_2O_4 nanoparticles (0.1 g) were added to HCl aqueous solution (0.1 M, 50 mL), and the mixture was treated with ultrasonication (KQ-100DE, China) for 10 min. After that, MnFe_2O_4 nanoparticles were separated and washed repeated with deionized water. Then, the treated MnFe_2O_4 nanoparticles were dispersed in a mixed solution of deionized water (20 mL), ethanol (80 mL), ammonia solution (25 wt%, 1.0 mL), and CTAB (0.3 g). The mixture was stirred for 30 min to form a uniform dispersion. TEOS (0.8 mL) was added dropwise to the mixture with constant stirring. After reaction for 6 h, the products were collected by a magnet and washed several times with ethanol and deionized water until the bubbles from the excess of CTAB disappeared entirely, and then dried under vacuum at 60°C for 8 h.

To investigate the role of CTAB in Cr(VI) removal, the extraction of CTAB in $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -CTAB composites was carried out. $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -CTAB composites (1.0 g) were dispersed in ethanol (150 mL, 95%) containing NH_4NO_3 (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 $\text{MnFe}_2\text{O}_4@\text{SiO}_2$.

2.3. Cr(VI) removal experiments

0.28 g of $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -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 H_2SO_4 or NaOH. After removal experiments, $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -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 MnFe_2O_4 , $\text{MnFe}_2\text{O}_4@\text{SiO}_2$, and $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -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 $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -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 (q_e) (mg/g) for Cr(VI) was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where C_0 and C_e (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 $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ -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 $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ 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 $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ 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 $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ 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 $K\alpha$ radiation. The specific surface area of $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ was determined by Brunauer-Emmett-Teller (BET) N_2 adsorption analysis using a surface area analyzer (Nova, 2000e; 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 $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ 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 $K\alpha$ radiation (1486.8 eV) under a residual pressure of 2×10^{-9} 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) ($\lambda_{\text{max}} = 540$ nm) (Wang et al., 2015). The concentration of residual total chromium in solution was measured using a flame atomic absorption spectrometer (AAS, Z-2000, 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 MnFe_2O_4 and $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$

Fig. 1 shows the XRD patterns of MnFe_2O_4 and $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$. The diffraction peaks of MnFe_2O_4 fit perfectly with the standard data of the spinel MnFe_2O_4 (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 MnFe_2O_4 , which are consistent with the results reported by previous research (Bao et al., 2013). These narrow sharp

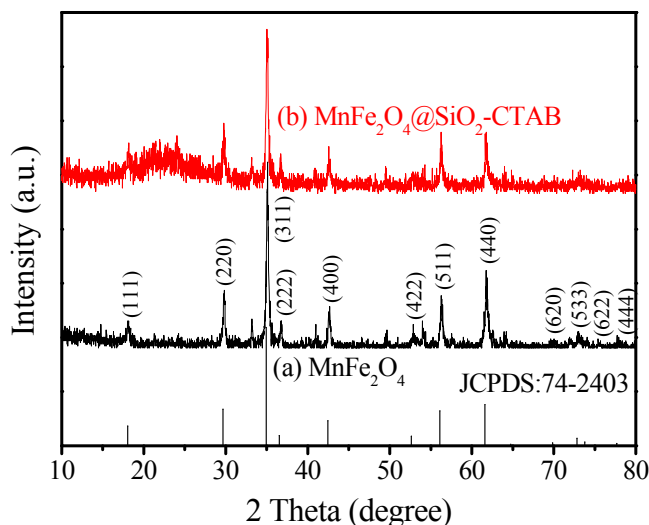


Fig. 1. XRD patterns of (a) MnFe_2O_4 and (b) $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$.

peaks demonstrated that MnFe_2O_4 particles were highly crystallized. The diffraction peaks of $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ composites (Fig. 1(b)) were similar to those of MnFe_2O_4 nanoparticles (Fig. 1(a)), indicating that MnFe_2O_4 nanoparticles were well retained in the modification process. $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ composites exhibited a broad peak at around $2\theta = 22^\circ$, which could be assigned to the mesoporous silica layer (Liu et al., 2014).

According to the SEM image of MnFe_2O_4 (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)), $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ composites displayed a typical core-shell structure. The outer shell was mesoporous silica with CTAB, while the core was MnFe_2O_4 nanoparticles. The thickness of mesoporous silica layer was about 100–150 nm. The silica layer can protect MnFe_2O_4 nanoparticles from corrosion and maintain the magnetism of MnFe_2O_4 , which was favorable to separate $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ composites from water.

The nitrogen adsorption/desorption isotherms and pore-size distribution of $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ 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/P_0) 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, $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ composites had a few systems of pores centered at 2.49, 3.92, 5.07, and 5.74 nm. This also proved that $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ composites were mesoporous materials. The specific surface area of $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$ composites was $53.4 \text{ m}^2/\text{g}$.

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 MnFe_2O_4 , $\text{MnFe}_2\text{O}_4\text{@SiO}_2$, and $\text{MnFe}_2\text{O}_4\text{@SiO}_2\text{-CTAB}$. 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

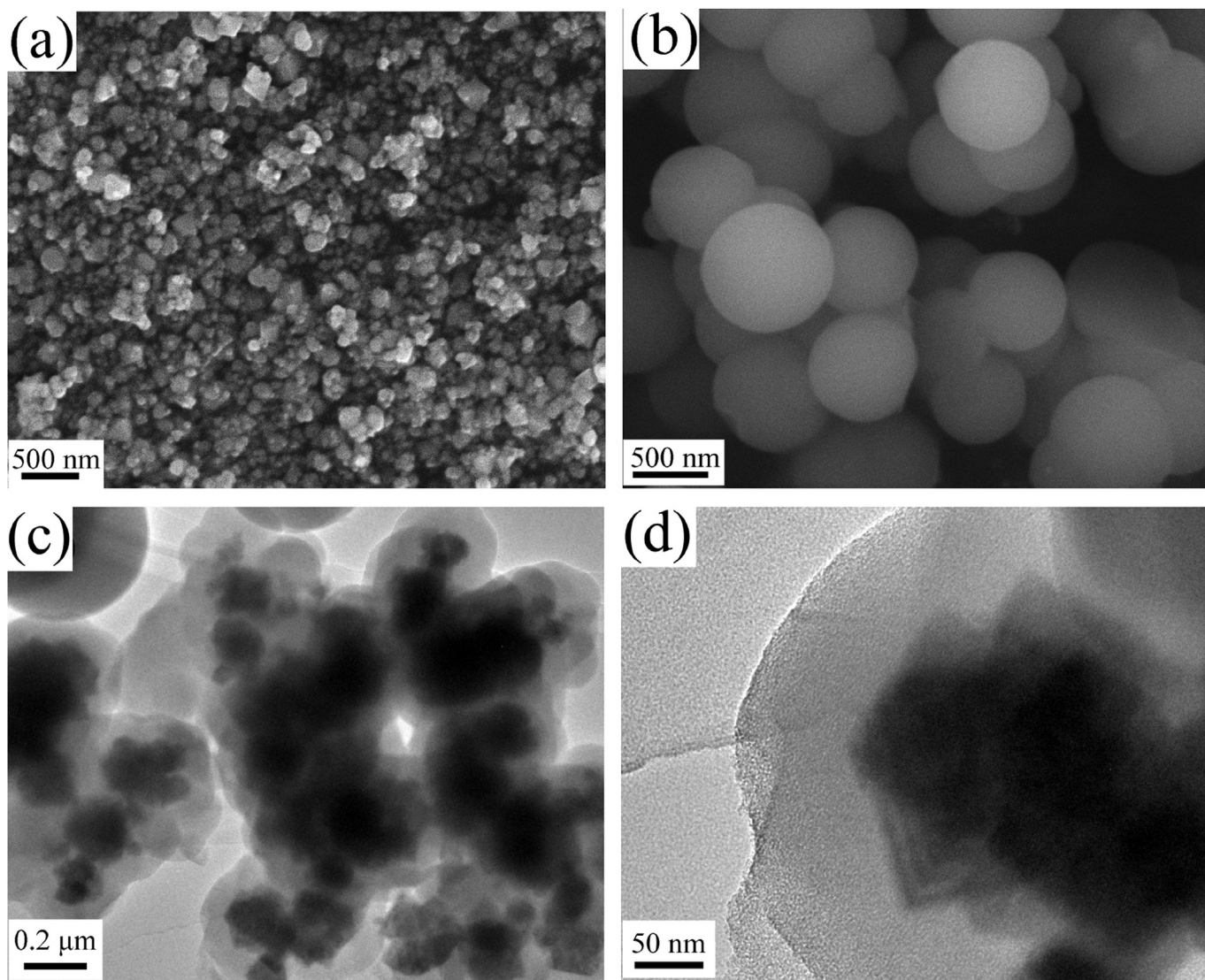


Fig. 2. The SEM images of (a) MnFe₂O₄ and (b) MnFe₂O₄@SiO₂-CTAB, and the TEM images ((c) and (d)) of MnFe₂O₄@SiO₂-CTAB.

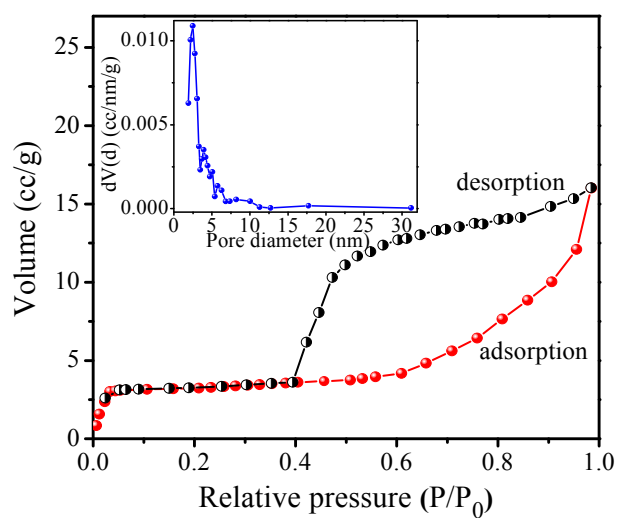


Fig. 3. Nitrogen adsorption/desorption isotherms of MnFe₂O₄@SiO₂-CTAB. Inset: Pore-size distribution of MnFe₂O₄@SiO₂-CTAB.

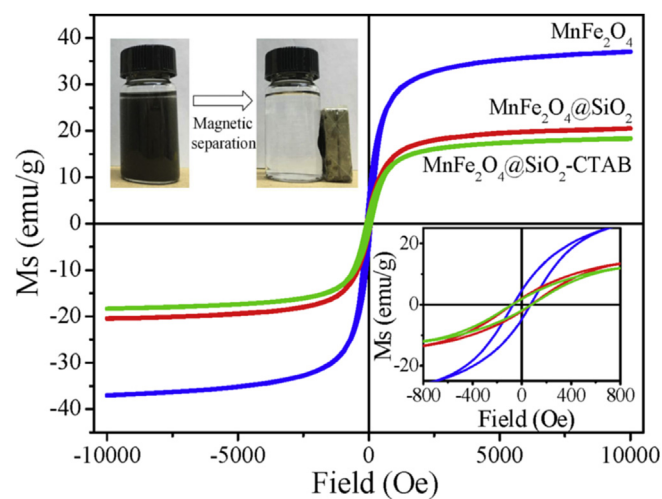


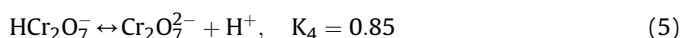
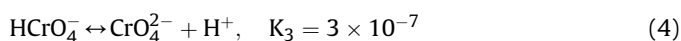
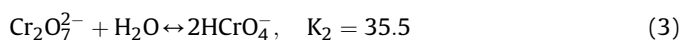
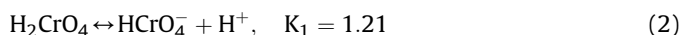
Fig. 4. Room-temperature magnetization curves of MnFe₂O₄, MnFe₂O₄@SiO₂, and MnFe₂O₄@SiO₂-CTAB. Inset: Magnified views of the hysteresis loops at low applied fields.

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 MnFe_2O_4 , $\text{MnFe}_2\text{O}_4/\text{SiO}_2$, and $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$, respectively. Since mesoporous silica and CTAB coated on MnFe_2O_4 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 $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ composites from aqueous dispersion using a magnet.

3.2. Cr(VI) removal by $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$

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

The performance of $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ 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 oxyanions of Cr(VI) are known to exist as described in the following equations (Eqs. (2)–(5)) (Xu et al., 2015).



At pH 3.0, the monovalent HCrO_4^- was the dominant species, while the HCrO_4^- converted to the divalent CrO_4^{2-} with the increase of pH value (Dinda and Saha, 2015). At low pH, the removal of Cr(VI) was through the adsorption of HCrO_4^- by $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ composites, but at high pH, the removal of Cr(VI) was mainly due to the adsorption of CrO_4^{2-} . There were a large number of CTA^+ cations existing on the $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ composites. The HCrO_4^- combined with CTA^+ cations ($\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$) and formed ion-pairs, but the divalent CrO_4^{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 $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ 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 $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$, contrast experiments on the effect of initial pH on the sorbate of Cr(VI) and adsorbent of $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ were performed separately (Fig. 1S) and discussed in Supplementary Material.

3.2.2. Comparative experiments among MnFe_2O_4 , $\text{MnFe}_2\text{O}_4/\text{SiO}_2$, and $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$

Comparative experiments of Cr(VI) removal among MnFe_2O_4 , $\text{MnFe}_2\text{O}_4/\text{SiO}_2$, and $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ were conducted. From Fig. 6, it can be seen that the performance of $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ composites in Cr(VI) removal was far better than that of MnFe_2O_4 and $\text{MnFe}_2\text{O}_4/\text{SiO}_2$. The fast and effective Cr(VI) removal was attributed to a high association rate between Cr(VI) and $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ 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 $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ 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 $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ 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 $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$, two well-known adsorption isotherm

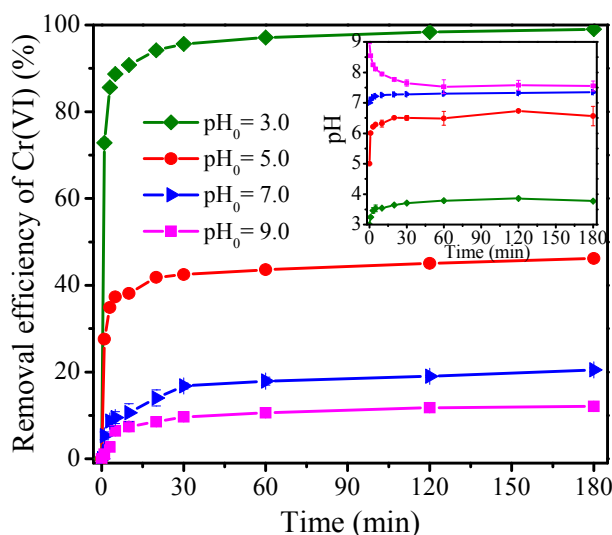


Fig. 5. Effect of initial pH on the Cr(VI) removal ($[\text{Cr(VI)}]_0 = 20.0$ mg/L, $[\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}]_0 = 2.8$ g/L). Inset: pH changes in the reaction process.

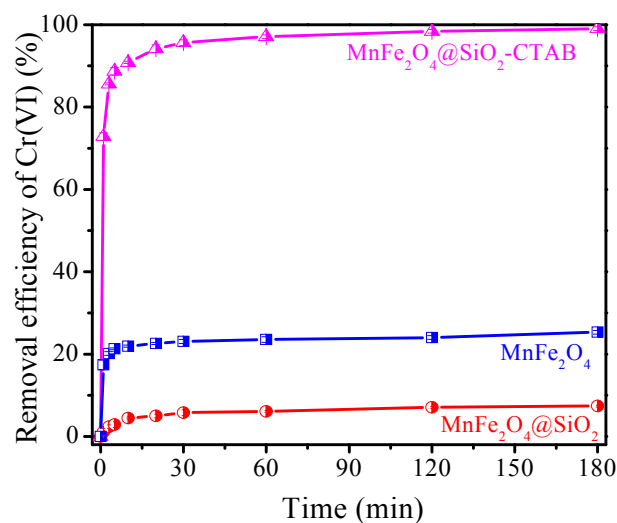


Fig. 6. Comparative experiments among MnFe_2O_4 , $\text{MnFe}_2\text{O}_4/\text{SiO}_2$, and $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ at pH 3.0 ($[\text{Cr(VI)}]_0 = 20.0$ mg/L, $[\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}]_0 = [\text{MnFe}_2\text{O}_4/\text{SiO}_2]_0 = [\text{MnFe}_2\text{O}_4]_0 = 2.8$ g/L).

models, the Langmuir (Eq. (6)) and Freundlich (Eq. (7)) isotherm equations were employed in the study (Wang et al., 2015).

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (6)$$

$$q_e = K_F C_e^{1/n} \quad (7)$$

Where q_e and $q_{\max}$ are the amount of Cr(VI) adsorbed at equilibrium and the maximum adsorption capacity (mg/g), respectively; K_L 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 $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ are shown in Fig. 7, and the related model parameters are presented in Table 1S. The maximum adsorption capacity (q_m) of $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ is 25.044 mg/g. The higher correlation coefficients ($R^2 = 0.994$) of Freundlich model indicated that the adsorption of Cr(VI) onto $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ 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 $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ 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.

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

Where q_t and q_e (mg/g) are the amounts of Cr(VI) adsorbed on $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ 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 $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$, $\text{MnFe}_2\text{O}_4/\text{SiO}_2$, and MnFe_2O_4 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 $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ 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 $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ composites phase. For the individual elemental mapping, the Mn, Fe, Si, and O elements showed similar mapping, demonstrating once again that MnFe_2O_4 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 $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ composites after reaction.

3.4.2. FT-IR analysis

The FT-IR spectra of $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ and Cr loaded $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$ are shown in Fig. 9. $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$

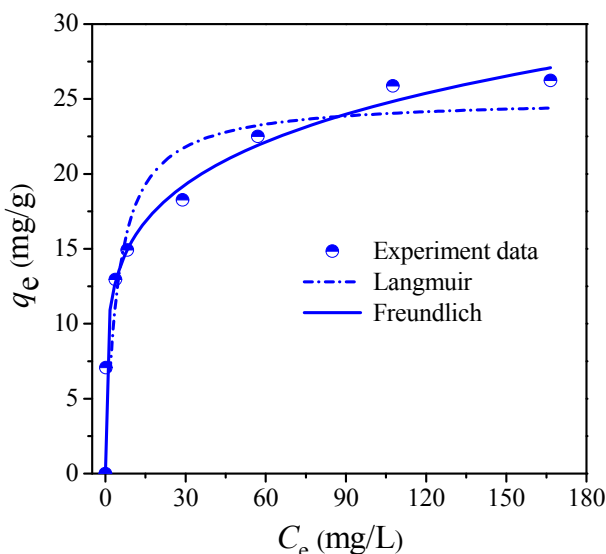


Fig. 7. Fitted adsorption isotherms of Cr(VI) on $\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$.

Table 1

The pseudo-first-order and pseudo-second-order kinetic parameters for the removal of Cr(VI) at initial Cr(VI) concentration of 20.0 mg/L.

Adsorbents	pH	Pseudo-first-order				Pseudo-second-order		
		$q_{e,\text{exp}}$ (mg/g)	k_1 (1/min)	$q_{e,\text{cal}}$ (mg/g)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e,\text{cal}}$ (mg/g)	R^2
$\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$	3.0	7.074	0.328	6.861	0.970	0.200	7.053	0.999
$\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$	5.0	3.299	0.594	3.125	0.938	0.158	3.333	0.999
$\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$	7.0	1.463	2.172	1.149	0.917	0.103	1.482	0.997
$\text{MnFe}_2\text{O}_4/\text{SiO}_2\text{-CTAB}$	9.0	0.863	13.033	1.099	0.985	0.102	0.913	0.999
$\text{MnFe}_2\text{O}_4/\text{SiO}_2$	3.0	0.528	5.122	0.469	0.993	0.301	0.546	0.997
MnFe_2O_4	3.0	1.809	0.367	1.667	0.900	0.307	1.786	0.998

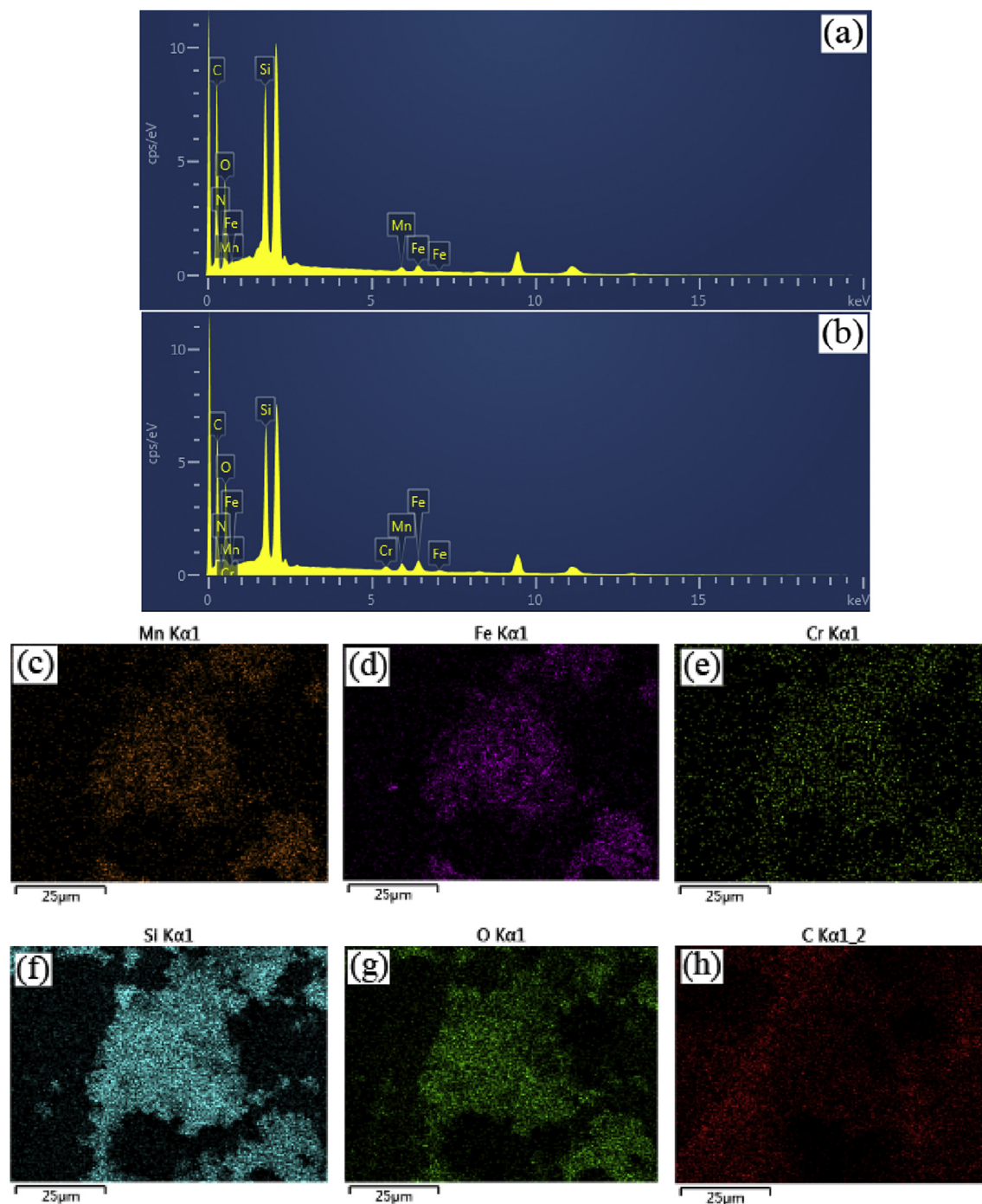


Fig. 8. The EDS spectra of (a) MnFe₂O₄@SiO₂-CTAB and (b) Cr loaded MnFe₂O₄@SiO₂-CTAB, SEM mapping of (c) Mn, (d) Fe, (e) Cr, (f) Si, (g) O, and (h) C in MnFe₂O₄@SiO₂-CTAB after reaction.

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 –CH₂– 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

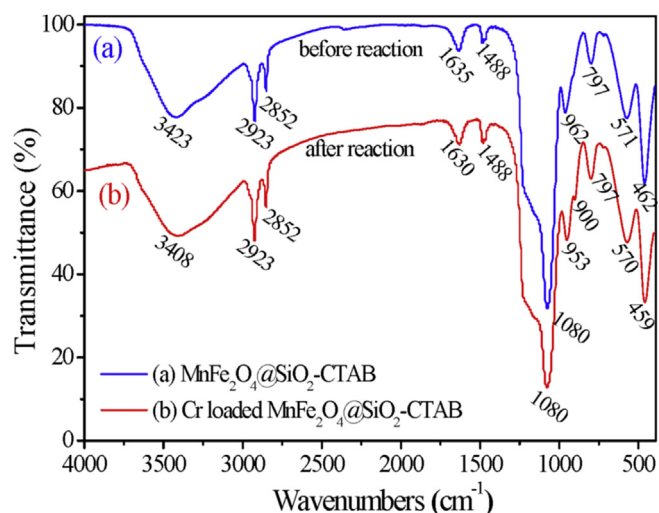


Fig. 9. FT-IR spectra of (a) $\text{MnFe}_2\text{O}_4@\text{SiO}_2\text{-CTAB}$ and (b) Cr loaded $\text{MnFe}_2\text{O}_4@\text{SiO}_2\text{-CTAB}$.

$\text{MnFe}_2\text{O}_4@\text{SiO}_2\text{-CTAB}$ composites and Cr species.

3.4.3. XPS analysis

Fig. 10 shows the XPS patterns of Cr $2p_{3/2}$, Mn $2p_{3/2}$, and O $1s$ of $\text{MnFe}_2\text{O}_4@\text{SiO}_2\text{-CTAB}$ before and after reaction. Cr XPS peak appeared after reaction (Fig. 10(a)). Cr $2p_{3/2}$ 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 $\text{MnFe}_2\text{O}_4@\text{SiO}_2\text{-CTAB}$ composites after reaction. Moreover, the Cr $2p_{3/2}$ peak at 577.1 eV indicated the formation of $\text{Cr}(\text{OH})_3$ in the process of reaction (Fu et al., 2015). The presence of Cr(VI) was attributed to the adsorption of Cr(VI) by $\text{MnFe}_2\text{O}_4@\text{SiO}_2\text{-CTAB}$ 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 $\text{Cr}(\text{OH})_x$ 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 $\text{Cr}(\text{OH})_3$ precipitates on $\text{MnFe}_2\text{O}_4@\text{SiO}_2\text{-CTAB}$ composites.

As shown in Fig. 10(b), the XPS spectra of Mn $2p_{3/2}$ 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 $\equiv\text{Mn}(\text{II})$ species on the surface of MnFe_2O_4 could act as reductants to transfer Cr(VI) into Cr(III). The reduction property of MnFe_2O_4 was also reported by previous research (Hu et al., 2007). With the reduction of Cr(VI), the H^+ ions in mixing solution were consumed, which caused an ascendant of pH value in acidic reaction condition (Inset of Fig. 5).

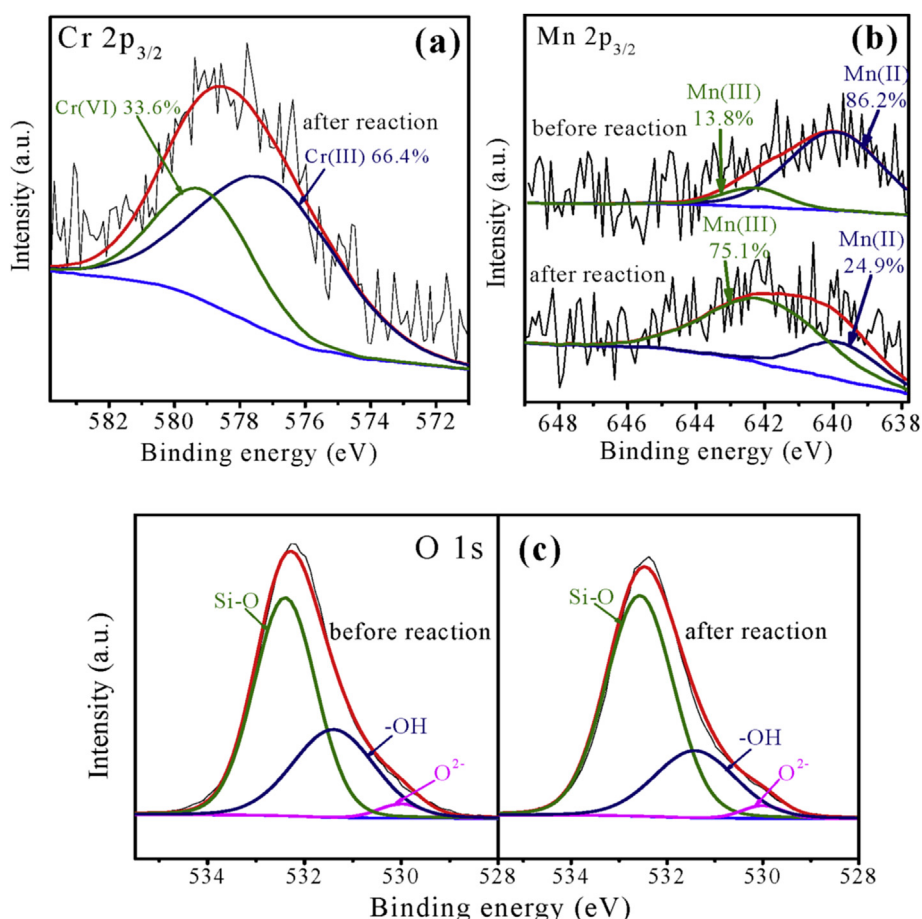
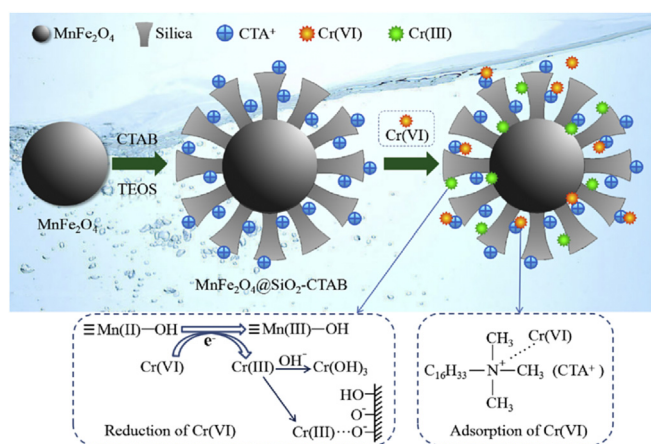
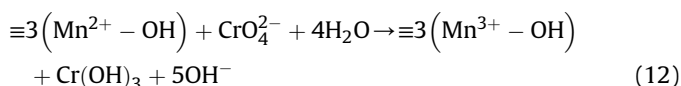
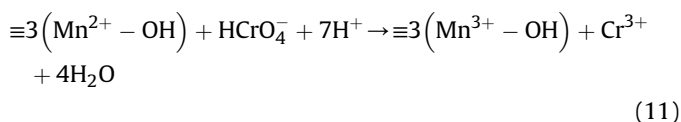
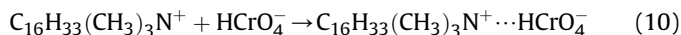


Fig. 10. XPS patterns of (a) Cr $2p_{3/2}$, (b) Mn $2p_{3/2}$, and (c) O $1s$ of $\text{MnFe}_2\text{O}_4@\text{SiO}_2\text{-CTAB}$ before and after reaction.

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, $MnFe_2O_4$ surface (Yao et al., 2014), and the adsorbed water molecules on $MnFe_2O_4@SiO_2$ –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 $MnFe_2O_4@SiO_2$ –CTAB composites exhibited a great potential for effective removal of Cr(VI) from aqueous solution.

3.5. Removal mechanism of Cr(VI)

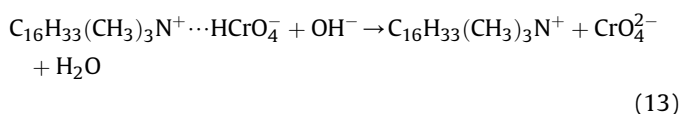
Based on the above discussion, the facile one-step modification route and the removal mechanism of Cr(VI) were illustrated in Scheme 1. The Cr(VI) removal occurred due to two aspects. First, mesoporous $MnFe_2O_4@SiO_2$ –CTAB composites with abundant CTA^+ could adsorb Cr(VI) from aqueous solution effectively and rapidly as the $HCrO_4^-$ (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 $MnFe_2O_4$. The electrons transferred from $\equiv Mn(II)$ species of $MnFe_2O_4$ 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 $MnFe_2O_4@SiO_2$ –CTAB composites in alkaline medium as shown in Eq. (12). The generated Cr(III) was immobilized via surface complexation and precipitation.



Scheme 1. The modification route and Cr removal mechanism of $MnFe_2O_4@SiO_2$ –CTAB.

3.6. Regeneration and reuse of $MnFe_2O_4@SiO_2$ –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 $MnFe_2O_4@SiO_2$ –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 $MnFe_2O_4@SiO_2$ –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 $MnFe_2O_4$.



4. Conclusions

Magnetic mesoporous composites ($MnFe_2O_4@SiO_2$ –CTAB) with novel core-shell structure were first prepared, characterized, and applied to remove Cr(VI). $MnFe_2O_4@SiO_2$ –CTAB composites were prepared by a facile one-step modification method. $MnFe_2O_4$ (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. $MnFe_2O_4@SiO_2$ –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 $MnFe_2O_4$ 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 $MnFe_2O_4@SiO_2$ –CTAB composites were

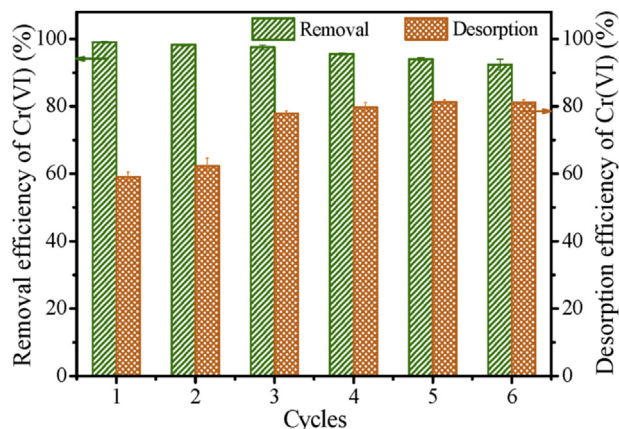


Fig. 11. The Cr(VI) removal and desorption efficiency during six cycles.

recyclable materials. From the above, the prepared $\text{MnFe}_2\text{O}_4\text{-SiO}_2\text{-CTAB}$ 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

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.10.097>.

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