Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

One-pot synthesis of C₁₈-functionalized core-shell magnetic mesoporous silica composite as efficient sorbent for organic dye Xiaole Zhang^{a,b}, Tao Zeng^a, Saihua Wang^a, Hongyun Niu^a, Xiaoke Wang^a, Yaqi Cai^{a,*}^a State Key Laboratory of Environmental Chemistry and Ecotoxicology of Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China^b College of Life Sciences, Hebei United University, Tangshan 063000, Hebei, China

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:

Received 11 December 2014

Accepted 10 February 2015

Available online 19 February 2015

Keywords:

Fe₃O₄/mSiO₂-C₁₈ nanocomposite

One-pot synthesis

Adsorption performance

Methylene blue

ABSTRACT

In this work, a facile one-pot strategy was proposed for the synthesis of C₁₈-functionalized core-shell magnetic mesoporous silica composite (Fe₃O₄/mSiO₂-C₁₈). The Fe₃O₄/mSiO₂-C₁₈ composite, with an average size of 80 nm and a functionalized mesoporous silica shell of about 30 nm in thickness, has excellent adsorption ability toward methylene blue dye (MB) due to the large surface area (303 m² g⁻¹) and the abundant hydrophobic C₁₈ groups. The adsorption equilibrium was achieved within 20 min and the adsorption behavior of MB on Fe₃O₄/mSiO₂-C₁₈ composite fitted the pseudo-second-order kinetic model well ($k_2 = 1.29 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$, $q_e = 144.72 \text{ mg g}^{-1}$, $h_o = 270.27 \text{ mg g}^{-1} \text{ min}^{-1}$ under 25 °C and an initial MB concentration of 10 mg L⁻¹). Langmuir and Freundlich isothermal adsorption models can both be used to describe the adsorption process and the maximum Langmuir adsorption capacity of MB on Fe₃O₄/mSiO₂-C₁₈ at 25 °C and pH 7.5 is 363.64 mg g⁻¹. Thermodynamic parameters show that the adsorption reaction is exothermic and spontaneous ($\Delta H^0 = -63.49 \text{ kJ mol}^{-1}$, $\Delta G^0 = -7.80 \text{ kJ mol}^{-1}$). Ionic strength and pH affected the adsorption slightly. In addition, the MB adsorbed sorbent can be readily separated from water solution by an external magnet because of the high magnetic saturation value (22.62 emu g⁻¹). After being regenerated by treatment with acidic methanol, the sorbent could be reused for at least 5 cycles with a little decrease in adsorption capacity.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Treatment of dye wastewater is always an important aspect of environmental pollution control because many dyes would bring health hazard toward humans and other lives and are difficult to degrade naturally in the environment [1–3]. Ordered mesoporous

* Corresponding author at: Chinese Academy of Sciences, Research Center for Eco-Environmental Sciences, P.O. Box 2871, Beijing 100085, China. Fax: +86 010 62849182.

E-mail address: caiyaqi@rcees.ac.cn (Y. Cai).

materials, as a kind of distinctive porous materials with huge surface area, uniform pore size distribution, and unique pore structure, have gained considerable interest in the removal of diverse dyes from water solutions [4]. Plenty of mesoporous materials, such as silica [5,6], carbon [7,8], TiO_2 [9,10], MgO [11,12], Cu_2O [13,14] and metal–organic framework (MOF) [15,16], have all been used as efficient sorbents for environmental remediation. Among them, mesoporous silica is the most widely-used one owing to the simple preparation, perfect chemical stability and biocompatibility [17,18]. Furthermore, the mesopore size can be easily controlled [19,20] and various functional groups can be modified onto the surface to obtain mesoporous silica with high adsorption selectivity toward different targets [21–24].

Recently, combination of ordered mesoporous silica with magnetic materials to synthesize novel magnetic mesoporous silica sorbents has attracted much attention. Zhao reported the preparation of $\text{Fe}_3\text{O}_4/\text{nSiO}_2/\text{mSiO}_2$ magnetic mesoporous silica microspheres for the adsorption of microcystin from water solution [25]. Based on it, magnetic mesoporous silica composites modified with different functional groups were synthesized for the adsorption removal of environmental pollutants [26–32] or extraction of trace hydrophobic organic pollutants [33,34] from aqueous matrix. These materials have ultrahigh adsorption performance toward targets due to the large surface area and unique pore structure of mesoporous silica. In addition, the magnetic portions endow the materials with magnetic separation ability so that the composites can be quickly isolated from aqueous solution with an external magnet after adsorption. Hence, the difficulty of solid–liquid separation for common nanoparticle sorbents is resolved and the treatment procedure is simplified greatly [28,33].

These researches have brought a new opportunity for the mesoporous sorbents in practical application. However, the preparation process of functionalized magnetic mesoporous silica sorbents is extremely complicated. A multiple-steps procedure including synthesis of magnetic nanoparticles (MNPs), coating of mesoporous silica, removal of template, and functionalization of the mesoporous silica shell is needed to obtain the final products. Moreover, the reaction conditions of some steps are harsh. These lead to a time-consuming synthesis process and relatively low yield, which severely limits the application of these materials in the treatment of dye wastewater. Therefore, development of facile synthesis method is necessary for the rapid popularization and practical application of these promising sorbents.

In this work, Fe_3O_4 MNPs were firstly synthesized through coprecipitation method in the presence of cationic surfactant. Next, a silica coat containing C_{18} functional groups, together with the surfactant, was fabricated onto the surface of Fe_3O_4 MNPs by the simultaneous hydrolysis of tetraethoxysilane (TEOS) and octadecyltriethoxysilane (ODS) in the same vessel. After the removal of the surfactant as soft template, C_{18} -functionalized mesoporous silica coated Fe_3O_4 MNPs ($\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$) were achieved. Thus, synthesis of Fe_3O_4 MNPs and coating of functionalized mesoporous silica shell were carried out in a single container through the method above mentioned.

The proposed method greatly simplified the synthesis procedure of functionalized magnetic mesoporous silica sorbents, which enable the rapid and large scale synthesis of these composites and promotes the application of them in adsorption removal of organic dyes from water solution. The adsorption performance of the $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ magnetic composites obtained through this one-pot method was investigated with methylene blue (MB) as a model target. To the best of our knowledge, the one-pot synthesis of functionalized magnetic mesoporous silica composites for the adsorption removal of organic dyes from water solution has not been reported.

2. Materials and methods

2.1. Materials

Octadecyltriethoxysilane was from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). Tetraethoxysilane (>98%) and methylene blue were obtained from Acros Organics (Morris Plains, NJ, USA). Ammonia aqueous solution (28%, W/W) was supplied by Alfa Aesar (Ward Hill, MA). LC-grade acetonitrile and methanol were from Fisher Scientific (Fair Lawn, NJ). Sodium hydroxide, $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, concentrated hydrochloric acid (37%, W/W), anhydrous ethanol, and hexadecyltrimethyl ammonium bromide (CTAB) were guarantee-grade reagents from Beijing Chemicals Co. Ltd. (Beijing, China). All reagents were used without further purification. Distilled water was prepared in the laboratory with a Milli-Q SP reagent water system from Millipore (Milford, MA).

2.2. One-pot synthesis of C_{18} -functionalized magnetic mesoporous silica composites

The synthesis procedure of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ nanocomposites is illustrated in Fig. 1(a). First, 0.1 g of NaOH and 0.5 g of CTAB were added to a mixture of anhydrous ethanol and distilled water (200 mL, V:V = 1:3) which was stirred for 0.5 h under 85 °C. Then, 5.0 mL of solution containing 0.1 g of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and 0.04 g of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ was added dropwise to the above mixture under vigorous agitation, followed by a further stirring for 0.5 h at 85 °C [35]. Next, the temperature of the reaction mixture was lowered to 60 °C and 60 mL of ethanol was added to the reaction mixture to get a proper solvent system for the sol–gel reaction. Subsequently, 0.6 mL of TEOS, together with different volume of ODS (0.05 mL, 0.15 mL, 0.3 mL, and 0.45 mL), were added successively within 20 min under ultrasonic treatment. After being stirred for another 0.5 h, the reaction matrix was cooled to ambient temperature and the products were isolated magnetically and rinsed with ethanol/concentrated hydrochloric acid (95/5, V/V) 3 times under ultrasonication to remove the template (CTAB). The obtained composites were washed with anhydrous ethanol to neutral pH, dried at 50 °C in a vacuum oven for 12 h, and signed with $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}\text{-1}$, $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}\text{-2}$, $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}\text{-3}$ and $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}\text{-4}$, respectively [36,37].

2.3. Materials characterization

The average size and morphology of the obtained $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ composites were observed with a Hitachi 7500 transmission electron microscope (TEM, Hitachi, Tokyo, Japan) operating at 80 kV. The successful coating of C_{18} -functionalized mesoporous silica shell was confirmed by the infrared (IR) spectra of the magnetic materials which were taken in KBr pressed pellets on a NEXUS 670 infrared Fourier transform spectrometer (Nicolet Thermo, Waltham, MA). Nitrogen sorption isotherms were measured at 77 K with a Quadrasorb™ SI Four Station Surface Area Analyzer and Pore Size Analyzer (Quantachrome Instruments, Boynton Beach, FL). Before measurement, the samples were degassed in a vacuum at 300 °C for at least 6 h. Brunauer–Emmett–Teller (BET) method was used to obtain the specific surface area with the adsorption data in a relative pressure range (P/P_0) of 0.05–1.0. By using the Barrett–Joyner–Halenda (BJH) model, the pore volume and pore size distribution were achieved from the adsorption branch of isotherm and the total pore volume (V_t) was estimated from the adsorbed amount at a relative pressure of 0.98 [25]. Low-angle X-ray diffraction (XRD) measurements were performed with a PANalytical X'pert Pro diffractometer (PANalytical, Almelo, the Netherlands), using a monochromatized X-ray beam with nickel-

Fig. 1. 'One-pot' synthesis procedure of C_{18} -functionalized magnetic mesoporous silica composites (a) and adsorption kinetic studies process (b).

filtered Cu K α radiation. A continuous scan mode was used to collect 2θ data from 0.5° to 9.0° with a $0.4^\circ \text{ min}^{-1}$ scan rate. Wide-angle XRD data were also collected from 10.0° to 90° with a scan rate of 4° min^{-1} [25]. The vibrating sample magnetization (VSM) curves of the magnetic materials were analyzed with an LDJ9600 magnetometer (LDJ Electronics, Troy, MI) by changing H between +10,000 and -10,000 Oe at 25°C .

2.4. Batch experiment and adsorption isotherm study

The batch experiment was conducted in 250-mL sealed glass Erlenmeyer flask containing 100 mL of aqueous solution with a sorbent dosage of 0.6 g L^{-1} . Ionic strength was controlled with 1.0 M NaCl solution and the initial solution pH was adjusted with 0.1 M of HCl and NaOH. The suspension was shaken at 150 rpm under 25°C for 6 h and the sorbent was isolated from solution with an external magnet. The residual concentration of MB in supernatant was measured with a Unico UV-4802S double-beam UV/visible spectrophotometer from Unico (Shanghai) Instrument Co., Ltd. (Shanghai, China) at the wavelength of 665 nm with distilled water as the reference.

The isothermal adsorption behavior of MB onto the $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ composite was studied by repeating the adsorption experiments at different temperature (25°C , 35°C and 45°C) and initial MB concentration (pH = 7.5 and 10 mM of NaCl). The adsorption isotherms of MB onto the sorbent at different temperature were obtained from the equilibrium adsorption capacities (q_e , mg g^{-1}) at various equilibrium MB concentrations (C_e , mg L^{-1}). Here,

$$q_e = (C_0 - C_e)V/m, \quad (1)$$

where C_0 (mg L^{-1}) is the initial concentration of MB, m (g) is the sorbent dosage, and V (L) is the adsorption volume [27].

The effect of solution pH was investigated in the pH range of 4.5–9.5 at the NaCl concentration of 10 mM and the influence of ionic strength, represented by NaCl concentration, was tested at

pH 7.5 (initial MB concentration: 10 mg L^{-1}). The final results are the average value of triplicate determination.

2.5. Adsorption kinetic study

Adsorption kinetic study was carried out according to the above adsorption procedure at pH 7.5 and 10 mM of NaCl. Here, 60 mg of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent were thoroughly mixed with 100 mL of MB solution with an initial concentration of 10 mg L^{-1} . The residual concentrations of MB in supernatant at certain time intervals (0.0–370 min) were determined by UV analysis after magnetic separation (Fig. 1(b)).

2.6. Regeneration and reusability studies of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent

Methanol, acidic methanol (methanol/concentrated HCl = 99/1, V/V), and acetonitrile were employed to desorb MB from $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent, respectively and the sorbent was isolated from aqueous solution magnetically after an ultrasonic radiation for 2 min. This desorption procedure was performed for another 2 cycles and the eluates were put together to determine the total desorption amount of MB dye. The desorption ratios calculated from the initial adsorption amount and the total desorption amount were used to select the proper eluant. The regenerated sorbent was recovered by magnetic separation and utilized to conduct the adsorption of MB for several cycles and the reusability of the sorbent was evaluated by the maximum adsorption capacities [38].

3. Results and discussions

3.1. Optimization of the synthesis of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ magnetic composite

In the first step, Fe_3O_4 MNPs were obtained through a modified hydrothermal coprecipitation method to meet the requirement of rapid synthesis. The ultrafine size also help to achieve a final $\text{Fe}_3\text{-}$

O_4/mSiO_2 nanosphere with a thicker mesoporous silica shell which can load more C_{18} -functional groups for adsorption. But the ultrafine Fe_3O_4 MNPs prepared with traditional coprecipitation method tend to aggregate seriously (see Fig. S1) and tedious and time-consuming separation, washing and modification are needed for the subsequent coating of mesoporous silica shell. In this work, cationic surfactant (CTAB) was introduced into the reaction system to improve the situation by forming positive micelle phase on the surface of Fe_3O_4 MNPs. However, CTAB in water solution would result in plenty of foam under vigorous agitation during the reaction. Therefore, ethanol was added to the mixture to prevent the forming of foam. Furthermore, the added CTAB and ethanol can also act as soft template and solvent respectively in the next simultaneous sol-gel polymerization for coating of mSiO_2 shell.

In the second step, functionalized mesoporous silica shell was fabricated on the surface of the Fe_3O_4 NPs through simultaneous sol-gel polymerization [34] directly in the reaction system of the first step without the necessity of boring separation and washing, so that lots of time was saved. The polymerization combined the mesoporous silica shell fabrication and functionalization into one step, but essential optimization are necessary to increase the adsorption ability of the final material. First, the optimum consumption of TEOS was determined by the VSM of the $\text{Fe}_3\text{O}_4/\text{mSiO}_2$ MNPs (Fig. S2) prepared with different volume of TEOS (0.2 mL, 0.4 mL, 0.6 mL, and 0.8 mL). Less TEOS would reach a thinner mesoporous silica shell (see Fig. S3) which has fewer sites for loading functional groups on the sorbent. But excessive TEOS may lead to a too thick silica shell of the $\text{Fe}_3\text{O}_4/\text{mSiO}_2$ nanospheres and obvious decrease of the magnetic separation ability, which greatly hinders the isolation of the sorbent from aqueous solution. From the VSM curves of different $\text{Fe}_3\text{O}_4/\text{mSiO}_2$ MNPs, the saturation magnetization of the material with 0.6 mL of TEOS is 22.62 emu g^{-1} which is sufficient for magnetic separation. As a result, a TEOS consumption of 0.6 mL was chosen in the actual operation.

The influence of ODS consumption in the adsorption performance of the achieved $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ materials was also investigated through their isothermal adsorption behaviors (Fig. 2) toward MB. From Fig. 2, we find that the adsorption ability of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent increases with the increasing consumption of ODS during synthesis. This is reasonable because higher consumption of ODS would result in more functional groups on the sorbent. But excessive ODS may lead to a high hydrophobic surface of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ composite, which hindered the dispersion of the sorbent into aqueous solution and the adsorption. Therefore, the adsorption ability of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}\text{-4}$ decreased slightly and a relatively poor dispersion of the sorbent in aqueous

solution was observed. Finally, $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}\text{-3}$ obtained with 0.3 mL ODS was chosen as the optimal magnetic composite for further studies.

3.2. Characteristics of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ magnetic composite

Compared with the Fe_3O_4 MNPs prepared with traditional coprecipitation method, the dispersion of CTAB modified Fe_3O_4 MNPs in solution was improved evidently (Fig. 3(a)) due to the electrostatic repulsion of the superficial positive micelle phase. The CTAB modified Fe_3O_4 MNPs shows basically spherical shape with uniform size of about 15 nm. After being coated with C_{18} -functionalized mesoporous silica layer, the typical core-shell structure of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs about 80 nm in diameter is discerned clearly (Fig. 3(b)). Several Fe_3O_4 particles are coated in an ordered mesoporous silica shell which is about 30 nm-in-thickness and possesses perpendicularly oriented channels.

Both the VSM curves of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs have little hysteresis and the remanence and coercivity are almost zero (Fig. S4), which indicate their typical superparamagnetic characteristic [39]. Compared with Fe_3O_4 MNPs, the saturation magnetization of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ magnetic composite decreases from 65.78 emu g^{-1} to 22.62 emu g^{-1} due to the introduction of non-magnetic mesoporous silica [40]. But it is still sufficient for the final sorbent to be isolated from aqueous solution magnetically. The superparamagnetism and high saturation magnetization of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ magnetic composite ensure that the sorbent can be dispersed thoroughly into water solution for the adsorption of dyes in the absence of external magnetic field, and can be separated rapidly from aqueous matrix after adsorption with a magnet. The N_2 sorption-desorption isotherm of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs (Fig. 4) exhibits an IV-type curve. A sharp peak of mesopore size distribution is observed for $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ microsphere (Fig. 4, inset) and the average mesopore size is 2.17 nm. The BET surface area and total pore volume are $303 \text{ m}^2 \text{ g}^{-1}$ and $0.382 \text{ cm}^3 \text{ g}^{-1}$, respectively, which is consistent with the characteristics of mesoporous materials [40].

In the wide-angle XRD pattern of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs (Fig. S5), the characteristic diffraction peaks of Fe_3O_4 MNPs are also present at 2θ of 30.1° , 35.5° , 43.1° , 53.4° , 57.0° and 62.6° , which are marked by their indices [(220), (311), (400), (422), (511) and (440)] [25]. But the intensity of these characteristic diffraction peaks are weakened because of the shielding effect of the C_{18} -modified mesoporous silica shell and the diffraction peak of amorphous mesoporous silica appears at 2θ of 23° . In the low-angle XRD pattern of the $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs, an obvious diffraction peak at 2θ of 2.4° reveals the short-range mesoscopic ordering characteristic (Fig. S5, inset) [25]. The pore size of the mesoporous silica shell is calculated to be 2.4 nm through Scherrer-equation, which is consistent with the results of TEM and BET.

From the IR spectra of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs (Fig. S6), we find that a strong absorption peak around 1080 cm^{-1} assigned to the Si-O-Si bond appears for the $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs. While the absorption band of Fe-O groups at 560 cm^{-1} decreases obviously because of the mesoporous silica shell. In addition, the characteristic bands of saturated C-H stretching vibrations at 2851 and 2921 cm^{-1} are also observed for the $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs. These demonstrate the successful coating of the mesoporous silica shell functionalized with octadecyl group [41].

3.3. Effect of solution pH and ionic strength

The adsorption capacities of MB on $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs at different pH are shown in Fig. S7(a). Since the hydrophobic interaction between the C_{18} groups and the organic dye molecules is the

Fig. 2. The adsorption abilities of different $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ magnetic composites toward MB at 35°C .

Fig. 3. TEM of CTAB modified Fe_3O_4 (a) and $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs (b).

Fig. 4. N_2 sorption-desorption isotherms and mesopore size distribution (the inset) of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs.

principal contributor for the adsorption, decreased adsorption capacity of MB on the $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent was observed at lower pH due to the weakened hydrophobic property of the cationic MB at lower pH [42]. However, the influence of solution pH on the adsorption of MB is insignificant in the pH range of 4.5–9.5 because the change of hydrophobic property of MB molecule in this pH range is un conspicuous. The adsorption capacity of MB on $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs at pH higher than 7.5 decreases slightly perhaps owing to the instability of the loading C_{18} functional groups on the sorbent at high pH [33]. As a result, pH 7.5 was selected for the following adsorption experiments.

Ionic strength would affect the surface charge density of sorbent and adsorbate, as well as the viscosity of solution, thus influence the adsorption of targets onto sorbent. Therefore, the effect of ionic strength on MB adsorption was investigated by conducting adsorption experiments at different NaCl concentrations at pH 7.5. Ionic strength only had a little influence on the adsorption of MB onto $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent and high adsorption capacity could be achieved even at the NaCl concentration of 100 mM (Fig. S7(b)). This suggests the potential application of the $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs in adsorption removal of dyes from aqueous solution with high salinity. Interestingly, small amount of inorganic ions facilitated the adsorption to a certain extent perhaps due to the enhancement of the hydrophobic interaction between the C_{18} functional groups and the organic molecules by the inorganic ions. In the following experiments, 10 mM of NaCl was added to the system to obtain higher adsorption efficiency.

3.4. Adsorption isotherm analysis and thermodynamic parameters

Langmuir equation and Freundlich equation were both used to describe the adsorption process of MB onto $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ composite. Langmuir model assumes that the adsorption process is monolayer adsorption on homogeneous surface without transformation and interaction between the adsorbed targets. While Freundlich equation is a semi-empirical model and is suitable for the adsorption onto heterogeneous surface at relatively low concentration.

$$\text{Langmuir equation: } q_e = q_m K_L C_e / (1 + K_L C_e), \quad (2)$$

$$\begin{aligned} \text{Rearranged Langmuir equation: } C_e/q_e \\ = 1/(q_m K_L) + C_e/q_m, \end{aligned} \quad (3)$$

$$\text{Freundlich equation: } q_e = K_F C_e^{1/n}, \quad (4)$$

$$\begin{aligned} \text{Rearranged Freundlich equation: } \log q_e \\ = \log K_F + (1/n) \log C_e, \end{aligned} \quad (5)$$

where q_m (mg g^{-1}) is the maximum adsorption capacity, K_L (L mg^{-1}) is the binding constant of MB onto $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent. K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and n are Freundlich adsorption constants, respectively [5].

The adsorption isotherms of MB onto the $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent and the fitting curves obtained with Langmuir model and Freundlich model are shown in Fig. 5 and the adsorption parameters are listed in Table 1. Regression coefficients (r^2) under different conditions are all higher than 0.95, indicating that both the models fit well with the MB adsorption. The maximum adsorption capacities of MB onto $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent obtained from Langmuir equation at 25 °C, 35 °C and 45 °C are 363.64 mg g^{-1} , 287.35 mg g^{-1} and 213.68 mg g^{-1} , respectively, with the adsorption equilibrium constants of 0.256 L mg^{-1} , 0.131 L mg^{-1} , and 0.127 L mg^{-1} . These values are superior to or comparable with those in most of the related works reported previously [10,22,30,42–46] except for the porous magnetic carbon sheet [47] (Table S1). The Freundlich adsorption intensity parameters are higher than 1.5, also demonstrating the strong adsorption trend of MB onto the sorbent. The maximum adsorption capacity and adsorption equilibrium constant both decrease with the rising temperature, indicating the exothermic reaction of the MB adsorption onto $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent and the higher adsorption efficiency at lower temperature.

Fig. 5. The adsorption isotherms (a) of MB onto the $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent and the fitting curves obtained with Langmuir model (b) and Freundlich model (c).

Table 1
Langmuir and Freundlich parameters at different temperatures.

Temperature (°C)	Langmuir model			Freundlich model		
	q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	r^2	K_F (mg ^{1-(1/n)} L ^{1/n} g ⁻¹)	n	r^2
25	363.64	0.256	0.982	74.12	1.689	0.991
35	287.35	0.131	0.960	35.07	1.662	0.986
45	213.68	0.127	0.972	27.06	1.652	0.954

The thermodynamic parameters of the adsorption process could be calculated from the following equations [5] for an initial MB concentration of 20 mg L⁻¹.

Equation of thermodynamic parameters:

$$\log(q_e/C_e) = \Delta S^0/2.303R - (\Delta H^0/2.303R)/T, \quad (6)$$

$$\text{Gibbs equation: } \Delta G^0 = \Delta H^0 - T\Delta S^0, \quad (7)$$

where ΔG^0 is the standard Gibbs free energy, ΔH^0 is the standard enthalpy change, ΔS^0 is the standard entropy change, T is the reaction temperature (K), and R is 8.314 J mol⁻¹ K⁻¹.

The $\log(q_e/C_e)$ and $1/T$ fit the equation of thermodynamic parameter well ($r^2 = 0.917$) and the ΔH^0 and ΔS^0 can be obtained from the slope and intercept of plot of $\log(q_e/C_e)$ versus $1/T$. The thermo-

dynamic parameters including ΔH^0 , ΔS^0 , and ΔG^0 at each temperature calculated through Gibbs equation are presented in Table 2.

From Table 2, it can be seen that the values of standard Gibbs energy (ΔG^0) at different temperatures are negative, indicating the spontaneous adsorption process of MB onto $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs. The lower ΔG^0 at higher temperature implies that the adsorption affinity and spontaneity decrease with the rising temperature. The negative ΔH^0 suggests the exothermic reaction of the adsorption, which is consistent with the experimental phenomenon. The value of ΔH^0 is -63.49 kJ mol⁻¹, which informs that chemisorption, perhaps originated from the oxygen-containing groups, exists between MB and $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs. The negative ΔS^0 (-186.88 J mol⁻¹ K⁻¹) shows that the solute molecule tends to be adsorbed onto the sorbent rather than to enter aqueous phase [5].

Table 2
Thermodynamic parameters^a of the adsorption process.

$\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$			$-\Delta G^0$ (kJ mol ⁻¹)		
ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)	r^2	at 25 °C	at 35 °C	at 45 °C
-63.49	-186.88	0.917	7.80	5.93	4.06

^a Solution pH: 7.5; NaCl concentration: 10 mM; sorbent consumption: 60 mg; initial concentration of MB: 20 mg L⁻¹.

3.5. Adsorption kinetic of MB onto $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs

The adsorption of target on ordered mesoporous materials is very fast because of the high surface area and short adsorption path so that the adsorption equilibrium can be achieved within a relatively short period of time. The adsorption kinetic curve of MB onto $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs (Fig. 6) indicates that about 95%

Fig. 6. The adsorption kinetic curve of MB onto $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs and the fitting curve with the pseudo-second-order kinetic model (the inset).

of MB adsorption happened during the first 10 min and the adsorption reached equilibrium after 20 min. The kinetics curve of MB adsorption was fitted using the pseudo-second-order model to describe the adsorption behavior quantitatively and calculate the kinetic parameters [42].

$$\text{Pseudo-second-order equation: } q_t = k_2 q_e^2 t / (1 + k_2 q_e t), \quad (8)$$

$$\text{Rearranged equation: } t/q_t = t/q_e + 1/k_2 q_e^2, \quad (9)$$

where k_2 ($\text{g mg}^{-1} \text{h}^{-1}$) is the rate constant of the pseudo-second-order adsorption, $k_2 q_e^2$ ($t \rightarrow 0$) is the initial adsorption rate (h_0 , $\text{mg g}^{-1} \text{min}^{-1}$), q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of MB adsorbed at equilibrium and t moment, respectively.

The linear plot of t/q_t versus t shows that the kinetic of MB adsorption onto $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ fits well with the pseudo-second-order kinetic model (Fig. 6, inset) with the linear regression (r^2) of 0.9999. Based on the slope and intercept of plot, the rate constant k_2 , equilibrium adsorption amount q_e , and initial adsorption rate $k_2 q_e^2$ are calculated to be $1.29 \times 10^{-2} \text{ g mg}^{-1} \text{h}^{-1}$, 144.72 mg g^{-1} , and $270.27 \text{ mg g}^{-1} \text{h}^{-1}$, respectively (initial MB concentration of 10 mg L^{-1} ; $T = 298 \text{ K}$).

3.6. Desorption of MB and the reusability of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent

Methanol, acidic methanol (methanol/concentrated HCl = 99/1, V/V), or acetonitrile were used as eluent to desorb MB from $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent and the results are shown in Fig. S8(a). It is worth noting that the desorption ability of acidic methanol is superior to those of methanol and acetonitrile. The small amount of HCl added obviously facilitated the desorption of cationic MB dye from the sorbent and almost all adsorbate was completely eluted by using 6.0 mL of acidic methanol (2.0 mL every time and washed 3 times). While no more than 78% of the adsorbate was recovered with equal amount of methanol or acetonitrile. As a result, acidic methanol was selected for the regeneration of sorbent.

After treatment with acidic methanol, the structure of sorbent was kept unchanged, suggesting the good stability of $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs during the regeneration process. Repeated adsorption experiments were performed to examine the reusability of the regenerated sorbent. After the sorbent was reused for five times, the decrease in maximum adsorption capacity of MB on $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent was no higher than 10% (Fig. S8(b)). This result indicates that the $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs could be successfully regenerated for reuse at least 5 cycles, which greatly saved the using cost.

4. Conclusion

In this research, superparamagnetic core-shell $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs were synthesized through a one-pot method and used for the adsorption removal of MB from water solution. The one-pot method employed greatly simplified the synthesis of functionalized magnetic mesoporous silica nanocomposites. The $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ composite exhibited ultrahigh adsorption capacity toward organic dyes owing to the high surface area of the mesoporous silica coat. In addition, the unique perpendicular channels of the mesoporous silica shell also provided a short adsorption path so that the adsorption equilibrium was achieved rapidly. The adsorption of MB onto $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ sorbent is a spontaneous exothermic reaction affected insignificantly by ions strength and solution pH. The magnetic sorbent could be recovered from aqueous matrix with an external magnet, which improved the convenience of operation significantly. The $\text{Fe}_3\text{O}_4/\text{mSiO}_2\text{-C}_{18}$ MNPs were successfully regenerated by treatment with acidic methanol and remained excellent adsorption ability toward MB after several reuse cycles. Anyway, we presented here a facile method for the preparation of a magnetic nanocomposite as an efficient sorbent with high adsorption performance and operation convenience for the removal of organic dyes from aqueous solution.

Acknowledgments

This work was jointly supported by the National Key Basic Research Program of China (2014CB114402), National Natural Science Foundation of China (21377034), China Postdoctoral Science Foundation funded project (2012M510573) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB14010201).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2015.02.029>.

References

- [1] Y.R. Zhang, S.L. Shen, S.Q. Wang, J. Huang, P. Su, Q.R. Wang, B.X. Zhao, *Chem. Eng. J.* 239 (2014) 250.
- [2] N. Bao, Y. Li, Z. Wei, G. Yin, J. Niu, *J. Phys. Chem. C* 115 (2011) 5708.
- [3] D.H. Reddy, S.M. Lee, *Adv. Colloid Interface Sci.* 201–202 (2013) 68.
- [4] Z. Wu, D. Zhao, *Chem. Commun.* 47 (2011) 3332.
- [5] C.H. Huang, K.P. Chang, H.D. Ou, Y.C. Chiang, C.F. Wang, *Microporous Mesoporous Mater.* 141 (2011) 102.
- [6] S. Wang, H. Li, *Microporous Mesoporous Mater.* 97 (2006) 21.
- [7] N. Mohammadi, H. Khani, V.K. Gupta, E. Amereh, S. Agarwal, *J. Colloid Interface Sci.* 362 (2011) 457.
- [8] V.K. Gupta, B. Gupta, A. Rastogi, S. Agarwal, A. Nayak, *J. Hazard. Mater.* 186 (2011) 891.
- [9] S. Asuha, X.G. Zhou, S. Zhao, *J. Hazard. Mater.* 181 (2010) 204.
- [10] R. Wang, X. Cai, F. Shen, *Appl. Surf. Sci.* 305 (2014) 352.
- [11] L. Ai, H. Yue, J. Jiang, *Nanoscale* 4 (2012) 5401.
- [12] C.L. Gao, W.L. Zhang, H.B. Li, L.M. Lang, Z. Xu, *Cryst. Growth Des.* 8 (2008) 3785.
- [13] J. Liu, Z. Gao, H. Han, D. Wu, F. Xu, H. Wang, K. Jiang, *Chem. Eng. J.* 185–186 (2012) 151.
- [14] Y. Shang, D. Zhang, L. Guo, *J. Mater. Chem.* 22 (2012) 856.
- [15] E. Haque, V. Lo, A.I. Minett, A.T. Harris, T.L. Church, *J. Mater. Chem. A* 2 (2014) 193.
- [16] A.X. Yan, S. Yao, Y.G. Li, Z.M. Zhang, Y. Lu, W.L. Chen, E.B. Wang, *Chem. Eur. J.* 20 (2014) 6927.
- [17] R. Vathyam, E. Wondimu, S. Das, C. Zhang, S. Hayes, Z. Tao, T. Asefa, *J. Phys. Chem. C* 115 (2011) 13135.
- [18] B.G. Trewyn, J.A. Nieweg, Y. Zhao, V.S.Y. Lin, *Chem. Eng. J.* 137 (2008) 23.
- [19] M. Thirumavalavan, Y.T. Wang, L.C. Lin, J.F. Lee, *J. Phys. Chem. C* 115 (2011) 8165.
- [20] M.E. Davis, *Nature* 417 (2002) 813.
- [21] Y.H. Kim, B. Lee, K.H. Choo, S.J. Choi, *Microporous Mesoporous Mater.* 138 (2011) 184.
- [22] K.Y. Ho, G. McKay, *K.L. Yeung, Langmuir* 19 (2003) 3019.
- [23] Z. Yan, S. Tao, J. Yin, G. Li, *J. Mater. Chem.* 16 (2006) 2347.

- [24] D. Carmona, F. Balas, J. Santamaria, *Mater. Res. Bull.* 59 (2014) 311.
- [25] Y. Deng, D. Qi, C. Deng, X. Zhang, D. Zhao, *J. Am. Chem. Soc.* 130 (2008) 28.
- [26] C. Wang, S.Y. Tao, W. Wei, C.G. Meng, F.Y. Liu, M. Han, *J. Mater. Chem.* 20 (2010) 4635.
- [27] J. Wang, S. Zheng, J. Liu, Z. Xu, *Chem. Eng. J.* 165 (2010) 10.
- [28] X. Fu, X. Chen, J. Wang, J. Liu, *Microporous Mesoporous Mater.* 139 (2011) 8.
- [29] G. Li, Z. Zhao, J. Liu, G. Jiang, *J. Hazard. Mater.* 192 (2011) 277.
- [30] Y. Tang, S. Liang, S. Yu, N. Gao, J. Zhang, H. Guo, Y. Wang, *Colloids Surf., A* 406 (2012) 61.
- [31] S. Tao, C. Wang, W. Ma, S. Wu, C. Meng, *Microporous Mesoporous Mater.* 147 (2012) 295.
- [32] F. Wang, Y. Tang, B. Zhang, B. Chen, Y. Wang, *J. Colloid Interface Sci.* 386 (2012) 129.
- [33] X.L. Zhang, H.Y. Niu, W.H. Li, Y.L. Shi, Y.Q. Cai, *Chem. Commun.* 47 (2011) 4454.
- [34] Z. Li, D. Huang, C. Fu, B. Wei, W. Yu, C. Deng, X. Zhang, *J. Chromatogr. A* 1218 (2011) 6232.
- [35] X. Zhang, H. Niu, Y. Pan, Y. Shi, Y. Cai, *Anal. Chem.* 82 (2010) 2363.
- [36] X. Liu, Y. Yu, M. Zhao, H. Zhang, Y. Li, G. Duan, *Food Chem.* 150 (2014) 206.
- [37] H. Liu, S. Ji, H. Yang, H. Zhang, M. Tang, *Ultrason. Sonochem.* 21 (2014) 505.
- [38] Y. Chi, W. Geng, L. Zhao, X. Yan, Q. Yuan, N. Li, X. Li, *J. Colloid Interface Sci.* 369 (2012) 366.
- [39] S. Huang, C. Li, Z. Cheng, Y. Fan, P. Yang, C. Zhang, K. Yang, J. Lin, *J. Colloid Interface Sci.* 376 (2012) 312.
- [40] O. Hakami, Y. Zhang, C.J. Banks, *Water Res.* 46 (2012) 3913.
- [41] Y. Liu, L. Jia, *Microchem. J.* 89 (2008) 72.
- [42] L. Lin, S.R. Zhai, Z.Y. Xiao, Y. Song, Q.D. An, X.W. Song, *Bioresour. Technol.* 136 (2013) 437.
- [43] M. Anbia, S.A. Hariri, *Desalination* 261 (2010) 61.
- [44] W.C. Chang, J.R. Deka, H.Y. Wu, F.K. Shieh, S.Y. Huang, H.M. Kao, *Appl. Catal., B* 142–143 (2013) 817.
- [45] C. Yan, C. Wang, J. Yao, L. Zhang, X. Liu, *Colloids Surf., A* 333 (2009) 115.
- [46] B.H. Hameed, A.L. Ahmad, K.N.A. Latiff, *Dyes Pigm.* 75 (2007) 143.
- [47] S. Zhang, M. Zeng, J. Li, J. Li, J. Xu, X. Wang, *J. Mater. Chem. A* 2 (2014) 4391.