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Sorption of carbamazepine from water by magnetic molecularly imprinted polymers based on chitosan-Fe_3O_4

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ABSTRACT

A novel magnetic-molecularly imprinted polymer (MMIP) based on chitosan-Fe_3O_4 has been synthesized for fast separation of carbamazepine (CBZ) from water. During polymerization, the modified chitosan-Fe_3O_4 was used not only as supporter but also as functional monomer. The properties of obtained MMIP were characterized by scanning electron and transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectra, thermo-gravimetric analysis and so on. The sorption equilibrium data was well described by Freundlich isotherm model and the increase in the temperature generated an increase in the sorption amount, indicating endothermic nature of adsorption process. Sorption kinetics followed the pseudo-second-order model. The feasibility of selective sorption of CBZ from real water by the MMIP was analyzed by using spiked real water samples. The result showed that the sorption capacity of MMIP has no obvious decrease in different water samples whereas there was obvious decline in the sorption amount of the MNIP.

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1. Introduction

The occurrence and effects of pharmaceuticals entering the environment has become a main environmental issue of global concern over the last decade (Salgado, Noronha, Oehmen, Carvalho, & Reis, 2010). Because of their high persistence, potentially toxic and low biodegradability, numerous pharmaceuticals and their derivatives have been increasingly detected in various environmental matrices. As one of the most studied pharmaceuticals, antiepileptic carbamazepine (CBZ) has been found in sewage treatment plants (STP) influent and effluent water (Metcalfe et al., 2003), surface water (Tixier, Singer, Oellers, & Muller, 2003; Zhou, Dai, Zhang, Surampalli, & Zhang, 2011), sediments, soils (Clara, Strenn, & Kreuzinger, 2004) and even frequently detected in drinking water (Benotti et al., 2009; Vulliet, Cren-Olive, & Grenier-Loustalot, 2011). Because of its resistance to biodegradation and stability, conventional municipal wastewater treatment plants are partially inefficient in removing CBZ (Zhang, Geissen, & Gal, 2008). Recently, molecular imprinting has been a useful technique in environmental field due to high selectivity of molecularly imprinted polymer (MIP) (Pichon, 2007; Pichon & Chapuis-Hugon, 2008). For instance, MIP has been applied to remove α-estradiol (Fernandez-Alvarez, Le Noir, & Guieysse, 2009), aniline (Lin et al., 2008), phenolic estrogens (Zhang & Hu, 2008), diclofenac (DFC) (Dai, Geissen, Zhang, Zhang, & Zhou, 2011), and CBZ (Jing et al., 2010) from contaminated and different sources water. Among the most applications of different morphology MIP, nanospherical MIP has a better performance for selective removal trace organic pollutant from environmental samples because its small particle size and high specific surface area could obtain a large amount of adsorption capacity and a fast adsorption rate. In our previous study, we prepared a nanosized double templates MIP to remove more than one pollutant in a different group together, and successfully use the MIP to selective remove CBZ and clofibric acid from water (Dai et al., in press). However, an outstanding drawback to nanosized MIP has restricted its widespread application that normal separation methods could not easily separate the nanosized MIP.

Attempts have been made to incorporate super paramagnetic iron oxide to the MIP and then withdrawn by application of an external magnetic field. Ansell and Mosbach (1998) prepared the (s)-propranolol imprinted magnetic copolymer beads using a suspension polymerization methodology in a perfluorocarbon liquid for the first time. Recently, the application of magnetic molecularly imprinted polymer (MMIP) for determination of fluoroquinolones(FQs) (Chen et al., 2010), sulfonamides (Chen et al., 2009b), tetracycline antibiotics (Chen et al., 2009a), bisphenol A (Ji et al., 2009), and endocrine disrupting chemicals (Li et al., 2010b) in real samples have been reported. For these studies, all the magnetic technology provides a rapid and easy way for separation of MMIP

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from complex matrix. Therefore, MMIP is viewed as a kind of potential sorbent. However, there are very few reports on application of MMIP to deal with the sorption of CBZ from environmental water samples, and the sorption behaviors and mechanisms of CBZ on MMIP have not been fully elucidated and understood. Thus, we suggested that using MMIP to fast separate CBZ from water by external magnetic field. It is important in water remediation to fast separate target pollutants from complex water bodies, which has scientific and economic significance.

In this study, a novel magnetic-molecularly imprinted polymer (MMIP) based on chitosan-Fe_3O_4 was synthesized by precipitation polymerization for the fast separation of carbamazepine (CBZ) from real water samples. To improve the stability and biocompatibility of the Fe_3O_4 nanoparticles, the supporter of MMIP was prepared by using chitosan-Fe_3O_4.The resulting chitosan-Fe_3O_4 was used not only as supporter but also as functional monomer. Polymerization was carried out in the presence of methacrylic acid (MAA) as assistant functional monomer, ethylene glycol dimethacrylate (EGDMA) as cross linker. The aim of the present study is to develop a fast way for selective separation of CBZ from real water samples. The characteristics of the MMIP and the sorption behaviors of the MMIP including sorption kinetics, isotherms and molecular recognition selectivity were investigated in detail.

Furthermore, the resulted MMIP was applied for selectively separation of CBZ from real water samples including tap water, river water and final sewage effluent water.

2. Materials and methods

2.1. Materials

Carbamazepine (CBZ), Diclofenac (DFC) sodium salt, methacrylic acid (MAA), divinylbenzene-80 (DVB-80), 2,2′-azobisisobutyronitrile (AIBN), Fe_3O_4 nanoparticles (30 nm outer diameters; 99.5% purity) were all obtained from Sigma–Aldrich Company. High performance liquid chromatography (HPLC) grade acetonitrile, methanol, toluene, phosphoric acid, glutaraldehyde (25%) as well as acetic acid were from Merck (Darmstadt, Germany). Analytical grade polyvinylpyrrolidone (PVP), ammonium hydroxide ($NH_3{\cdot}H_2O$), oleic acid, liquid paraffin, Span-80 and chitosan with 98% deacetylation and an average molecular weight of 6×10^4 g mol^{-1} were purchased from Sinopharm Chemical Reagent (Shanghai, China). Ultra–pure water was produced by a Milli-Q water purification system (Millipore, Bedford, MA, USA). AIBN was recrystallized in methanol prior to use.

Standard stock solutions of CBZ (200 m g L^{-1}) and DFC sodium salt (200 mg L^{-1}) were prepared in Millipore water and stored at 4 °C.

2.2. Preparation of chitosan modified Fe_3O_4 composite

Synthesis of the chitosan-Fe_3O_4 was based on previous study with some modification (Li, Jiang, Huang, Ding, & Chen, 2008). In a typical preparation of chitosan-Fe_3O_4, 0.5 g of chitosan flake dissolved in 50 mL of 3% (v/v) acetic solution, 0.2 g Fe_3O_4 nanoparticles were added into a three-necked flask. After ultrasonic dispersion for 30 min, 40 mL of liquid paraffin and 0.5 mL of Span-80 were added into the mixture under vigorously stirring at 30 °C. The solution's pH was adjusted to maintain a level of 8.0–9.0 by adding 25% (v/v) of $NH_3{\cdot}H_2O$ solution during the reaction. Then 2 mL of glutaraldehyde solution (25 wt %) was added into reaction flask and crosslinking reaction was kept for 1.5 h at 60 °C. The obtained magnetic chitosan was separated from the solution by using a permanent magnet and were washed by ethanol and deionized water in turn until pH was about 7 and then dried at 50 °C for further use.

2.3. Synthesis of the MMIP

The MMIP was synthesized by non-covalent binding (self-assembly) polymerization. The steps are as follows:

(1) Preparation of pre-assembly solution: 0.64 mmol of CBZ was dissolved in 10 mL of acetonitrile/toluene (75:25, v/v) in a vessel, and then 0.33 mL (3.89 mmol) of MAA was added and stirred for 30 min. (2) Preparation of pre-polymerization solution: 0.3 g of chitosan-Fe_3O_4 and 1.0 mL oleic acid was added into a reaction flask and stirred for 10 min. Then 1.82 mL (13.06 mmol) of cross-linker DVB-80 and the pre-assembly solution were both added into the mixture of magnetic chitosan and oleic acid, and stirred for 30 min. (3) The dispersant PVP (0.4 g), the pre-polymerization solution and AIBN (92.5 mg, 0.565 mmol) were added into 100 mL of acetonitrile/toluene (75:25, v/v) in a vessel. The mixture was stirred at 300 rpm and purged with nitrogen gas to displace oxygen while the temperature increased to 60 °C. The reaction was at 300 rpm and 60 °C for 24 h. (4) After polymerization, the resultant polymer was separated by using a permanent magnet and Soxhlet extracted with methanol/acetic acid (9/1, v/v) for 24 h for each cycle to remove the template (CBZ) and filtered. This procedure was repeated several cycles until CBZ could not be detected in the filtrate. The remaining MMIP was washed with methanol for three times to remove residual acetic acid. Finally, the microspheres were dried under vacuum at 60 °C for use in subsequent studies.

Additionally, the corresponding magnetic non-molecularly imprinted polymer (MNIP) was prepared in the same manner but without the template (CBZ) addition. What's more, the non-magnetic MIP was also prepared based on previous study (Beltran et al., 2007; Beltran, Marcé, Cormack, & Borrull, 2009; Jing et al., 2010), with some modification. Briefly, the MIP was synthesized by the same way with MMIP but without chitosan-Fe_3O_4, oleic acid and PVP addition. The non-molecularly imprinted polymer (NIP) was prepared in the same way for preparation of MIP but without the template (CBZ) addition.

2.4. Characterization of the MMIP

The images of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were observed on a VEGATS 5136 MM (TESCAN) and JEM 2011 (Jeol, Japan) microscopes, respectively. The specific surface areas and pore parameters of the polymers were measured by nitrogen sorption porosimetry performed on an ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer (Micromeritics Instrument Corporation, Norcross, GA). The specific surface area was calculated using the BET equation. The mesopores size distribution was determined by Barrett–Joyner–Halenda (BJH) method. The determination of the point of zero charge (pH_{pzc}) for the activated carbons was carried out as follows: 50 mL of 0.01 M NaCl solution was placed into each conical flask, and the solution pH was adjusted from 2 to 12 with 0.01 M HCl or NaOH solution. Thereafter, 0.15 g of MMIP or MNIP was added into each flask, and the flasks were sealed and shaken at 25 °C for 48 h. Finally, the equilibrium solution pH was measured. The pH point where $pH_{initial} = pH_{final}$ was taken as the pH_{pzc} of the polymers (Yu, Zhang, Deng, Huang, & Yu, 2009). Thermogravimetric analysis (TGA) was performed for powder samples (about 10 mg) using a Diamond TG/DTA instruments (PerkinElmer, USA) under a nitrogen atmosphere up to 700 °C with a heating rate of 5.0 °C min^{-1}. The crystalline phase of the composites was identified on a D8 Advance X-ray powder diffractometer (Bruker, Germany) using Cu Kα radiation. Fourier transform infrared (FT-IR) spectra was measured on a Nicolet 5700 spectrometer (Thermo, USA). The magnetic properties were measured on a vibrating sample magnetometer (VSM) (LakeShore, USA).

2.5. Binding experiment

For the binding kinetics experiments, 10 mg of MMIP or MNIP was suspended in 5 mL CBZ solution with an initial CBZ concentration of 100 mg L^{-1} and stirred at 200 rpm for measuring the binding efficiency as a function of time. For the binding isotherms experiments, a series of CBZ solutions (from 10 to 200 mg L^{-1}) was prepared. 5 mL of each solution and 10 mg of MMIP or MNIP was added to a 10-mL flask. The mixtures were shaken for 2 h at 25 °C and 35 °C, respectively. To investigate the selectivity of MMIP adsorbent, 10 mg of MMIP or MNIP were added to a 10 mL flask, each of which contained 5 mL mixture of CBZ (100 mg L^{-1}) and DFC (100 mg L^{-1}). To compare with the sorption abilities, 10 mg of MMIP, MNIP, non magnetic MIP, non magnetic NIP or chitosan were added to a 10 mL flask, each of which contained 5 mL of CBZ (100 mg L^{-1}). After shaken for 2 h, the MMIP and MNIP were isolated by a strong magnet and the MIP, NIP and chitosan were filtrated through 0.2 μm membrane filters (Millipore). The concentration of CBZ in the solvent phase was determined with HPLC.

The adsorption equilibrium data was fitted to Langmuir and Freundlich isotherm models. The equations were expressed as follows:

Langmuir equation:

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \quad (1)$$

where K_L is the Langmuir constant (L μmol^{-1}), Q_m is the maximum sorption capacity (μmol g^{-1}), C_e is the equilibrium concentration (μmol L^{-1}) of CBZ in aqueous solution.

Freundlich equation:

$$Q_e = K_F C_e^{1/n} \quad (2)$$

where K_F is the Freundlich constant (μmol g^{-1}) and n is an indication of the nonlinearity

The kinetic data obtained was analyzed using pseudo-first order and pseudo-second-order rate models. The pseudo-first-order equation can be expressed as Eq. (3).

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (3)$$

The pseudo-second-order equation can be expressed as Eq. (4).

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (4)$$

where Q_e (μmol g^{-1}) is the equilibrium capacity and Q_t (μmol g^{-1}) is the adsorption capacity at different time. t (min) is the sorption time. k_1 (L min^{-1}) and k_2 (g μmol^{-1} min^{-1}) are the rate constants of pseudo-first order and pseudo-second order adsorption.

2.6. Application of MMIP for separation of CBZ from real water samples

River water was collected from Huangpu River in Shanghai. Wastewater sample was from a sewage treatment plant in Shanghai and tap water was collected in the laboratory. All the water samples were kept in the dark at 4 °C and filtered with a cellulose acetate filter prior to use. Samples were spiked with 50 mg L^{-1} of CBZ. 10 mg of MMIP was mixed with 5 mL of spiked river water, wastewater, tap water and deionized water. The binding of CBZ to the MNIP was also carried out in the same way. All experiments were conducted in triplicate.

2.7. Regeneration/reuse of MMIP

An amount of 10 mg of MMIP was added to 5 mL CBZ spiked river water (50 mg L^{-1}). After being shaken for 2 h at room temperature, the mix was centrifuged at 5000 rpm for 5 min to remove the MMIP. Then, 0.5 mL of supernatant was analyzed by HPLC. The recovered MMIP was regenerated with 5 mL of methanol/acetic acid (9:1, v:v) followed by 5 × 1 mL of methanol, dried in vacuum, and reused in the next cycle of sorption experiments.

2.8. Analysis of CBZ

The concentration of CBZ was performed on an Agilent 1200 HPLC system (Agilent Technologies, USA) with diode array detector (DAD) and a SHIMADZU C18 reversed-phase column (250 mm × 4.6 mm, 5 μm). The mobile phase consisted of 60% mixture of methanol and acetonitrile (1:1, 0.1% acetic acid) and 40% purified (Millipore) water (0.1% phosphoric acid). The flow rate was 1.0 mL/min, and the sample volume injected was 20 μL. The detection wavelength was 230 nm. Samples were filtered through a 0.45 μm syringe filter (Millipore) before injection.

3. Results and discussion

3.1. Characterization of MMIP

Fig. 1 shows the scan electron microscopy (SEM) and transmission electron microscopy (TEM) images of MMIP and MNIP. The sizes of MMIP and MNIP microspheres are about 454 nm and 506 nm in diameter and roughly spherical shape, which is suitable for rebinding of template molecules. TEM image clearly shows the core–shell structure of polymers revealing the binding sites existed at the surface of MMIP, which can improve the mass transfer rate for rebinding and releasing the template molecules.

The specific surface areas and pore parameters of the polymers for MMIP and MNIP were listed in Table S1 ("S" indicates figure and table in the Supporting Information). They were 98.5 m^2 g^{-1}, 0.1058 cm^3 g^{-1}, 3.17 nm respectively, for MIP, while these parameters were not obviously different from those of MNIP. Therefore, the distinct adsorption properties for MMIP and MNIP could not entirely be attributed to the morphological differences, but to the imprinting effect. According to the IUPAC definition, MMIP and MNIP mainly possessed mesopores. Moreover, the average pore diameter for the MMIP was slightly higher than that of MNIP, also strongly indicating the imprinting effect. The resulted zero point charge of MMIP and MNIP were 4.64.

Fig. 1(c) and (d) compares the XRD patterns of the Fe_3O_4, chitosan-Fe_3O_4, MMIP, MNIP. In the 2θ range of 20–70°, six characteristic peaks for Fe_3O_4 (2θ = 30.2°, 35.5°, 43.1°, 53.4°, 57.0°, and 62.6°) were all observed in chitosan-Fe_3O_4, MMIP and MNIP, and the peak positions could be indexed to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) (JCPDS card (19-0629)). The result reveals that the crystal structure of Fe_3O_4 remained stable in the polymerization process and the Fe_3O_4 was indeed incorporated into MMIP and MNIP (Kan, Geng, Zhao, Wang, & Zhu, 2009).

Fig.S1 shows the FT-IR spectra of MMIP and MNIP. The peaks at 577 cm^{-1} were assigned to Fe—O bond vibration of Fe_3O_4, which suggests the Fe_3O_4 was successfully packed into the polymer.The adsorption peak at 2926 cm^{-1} are ascribed to C—H band. In addition, MMIP and MNIP showed the absorption bands at 1666 cm^{-1} and 1669 cm^{-1}, respectively, which were assigned to N—H stretching vibration. There is an apparent shift in the frequencies of IR spectra, the O—H band vibration was 3432 cm^{-1} of MMIP compared with 3356 cm^{-1} of MNIP, which can be attributed to the presence of the hydrogen bonding in MMIP. Compared to the major peaks for chitosan-Fe_3O_4 (Fig.S1), the FT-IR spectrum of the MMIP and MNIP demonstrated that the chitosan-Fe_3O_4 was successfully cross-linked with the polymer due to their similar peaks.

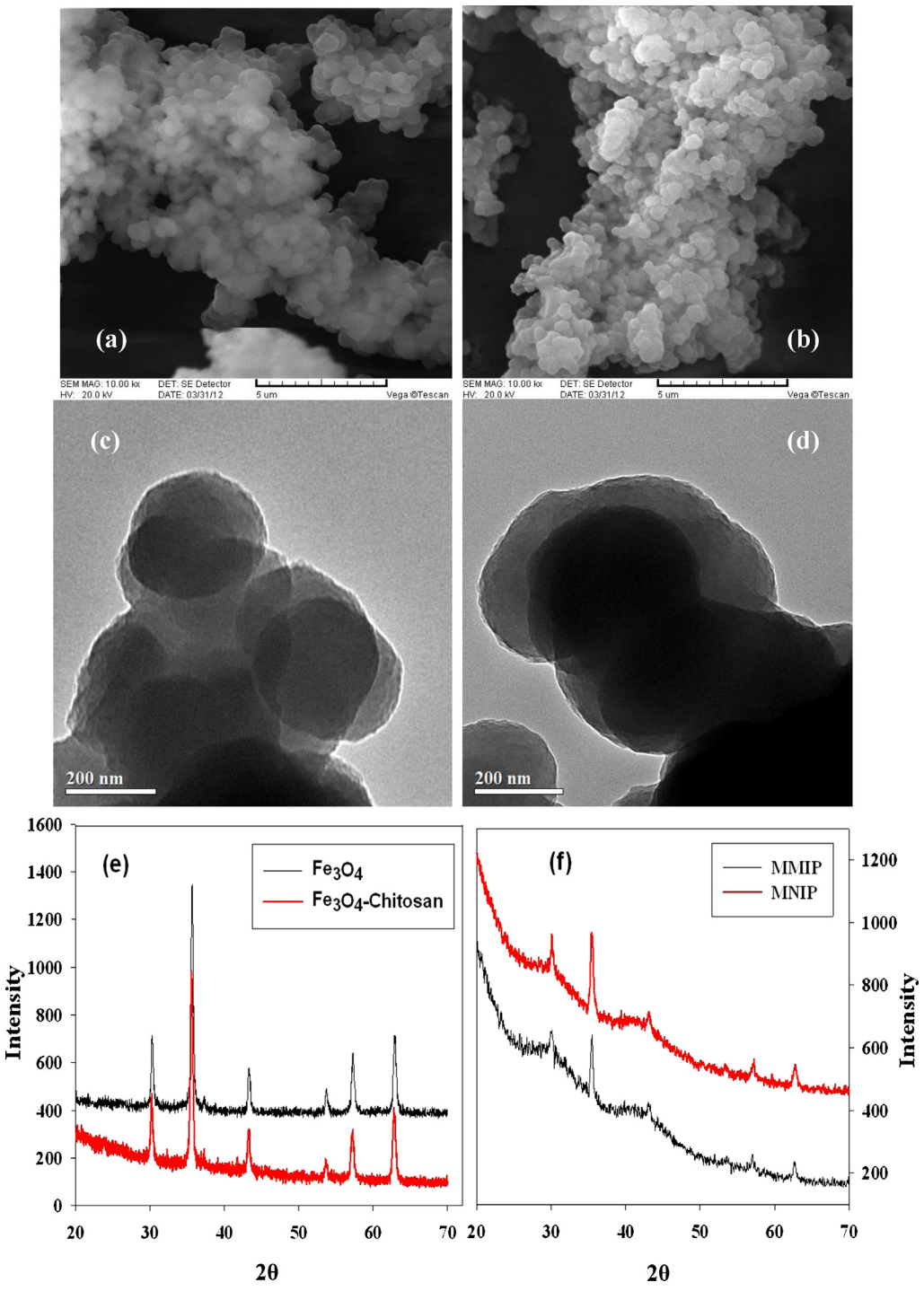

Fig. 1. The SEM and TEM micrographs of the MMIP (a and c) and MNIP (b and d); XRD patterns of Fe_3O_4 and chitosan-Fe_3O_4 (e),and MMIP and MNIP (f).

The thermo-gravimetric analysis (TGA) was applied to quantify the weight percentages of Fe_3O_4 embedded in chitosan-Fe_3O_4, MMIP and MNIP. Fig. 2 shows the TGA curves of Fe_3O_4, chitosan-Fe_3O_4, MMIP and MNIP. For Fe_3O_4, the TGA curve shows that the weight loss over the temperature ranged from 30 °C to 700 °C was about 5%. This might be due to the loss of residual water in the sample. For chitosan-Fe_3O_4, MMIP and MNIP, the weight loss of all the particles were quite small below 200 °C,which can be ascribed to the loss of residual water for each particle. When the temperature was raised to higher than 600 °C, the weight loss was significant because the decomposition of polymers. There was no significant weight change from 600 °C to 700 °C, indicating the presence of only Fe_3O_4 within the temperature range. From the percentage weight loss in the TGA curves, the amount of Fe_3O_4 in chitosan-Fe_3O_4, MMIP and MNIP were estimated about 29.2%, 17.1% and 15.9%, respectively.

The magnetic properties of chitosan-Fe_3O_4, MMIP and MNIP were investigated with a VSM. Fig. 3a and b show that the magnetization curves of three samples were no hysteresis and symmetrical about the origin, suggesting that the samples were super-paramagnetic, which facilitated magnetic separation and reusability. The saturation magnetization (Ms) values

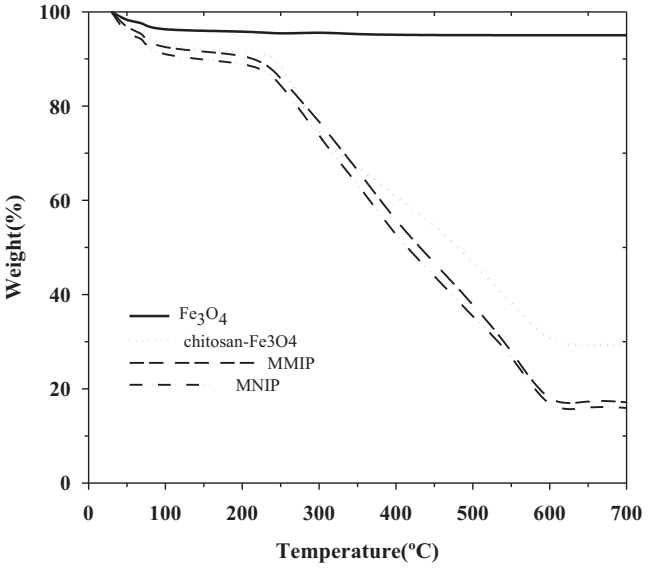

Fig. 2. Thermo-gravimetric analysis of the Fe_3O_4, chitosan-Fe_3O_4, MMIP and MNIP.

obtained at room temperature were 13.5 emu g^{-1}, 1.8953 emu g^{-1} and 1.7012 emu g^{-1} respectively. This result agreed with the experiments of thermo-gravimetric analysis. The decrease in magnetization value was expected because the polymeric coating had effectively shielded the magnetite. Though with low Ms value, the results from Fig. 3c suggested that the remained magnetic force in MMIP could meet the need of magnetic separation by an external magnetic field. The results also illustrated that MMIP was a feasible magnetic separation carrier. The obtained Ms value of MMIP

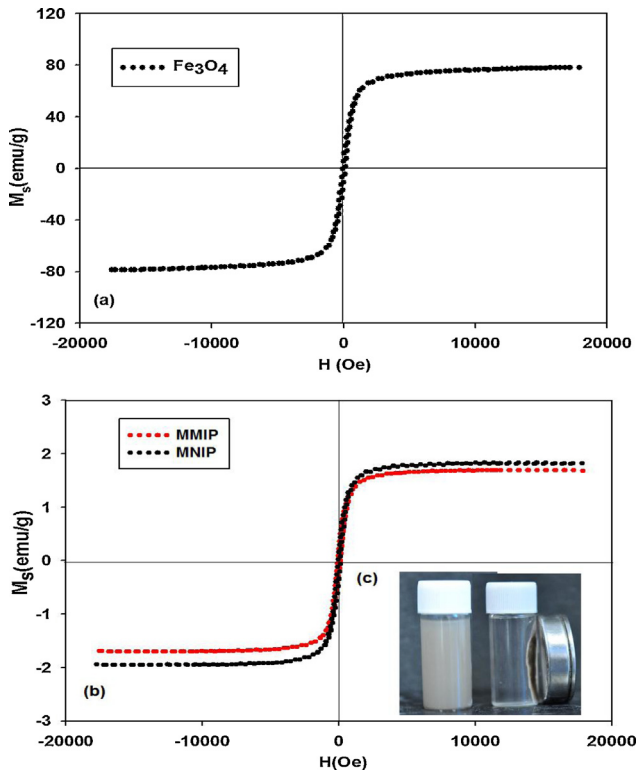

Fig. 3. Magnetic hysteresis loops of chitosan-Fe_3O_4 (a), MMIP and MNIP (b), and a photograph of MMIP dispersed in water in the presence (right) and absence (left) of an external magnetic field (c).

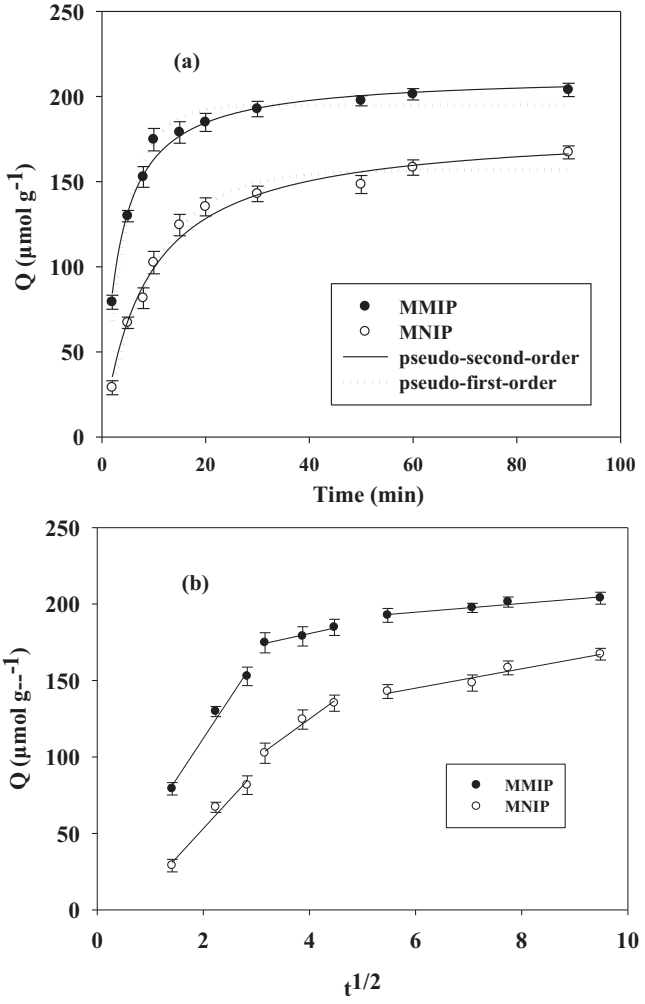

Fig. 4. (a) Adsorption kinetics and (b) intraparticle diffusion models for the sorption of CBZ on the MMIP and MNIP. Adsorbents dose: 10 mg, initial CBZ concentration: 100 mg L^{-1}, solution volume: 5 mL, contact time: 2 h.

was relatively high and satisfactory when compared to those from previous works (Dai et al., 2012; Ding et al., 2011; Li et al., 2010a; Yang et al., 2012), where the Ms values of MMIP were 1.68 emu g^{-1}, 0.69 emu g^{-1} and 0.41 emu g^{-1}, 1.57 emu g^{-1}, respectively.

3.2. Binding kinetics

Fig. 4a shows the sorption kinetics of the MMIP and MNIP adsorbents for CBZ. Obviously, the sorption amount of the MMIP particles for CBZ was higher than the MNIP particles, suggesting the good imprinting effect of the MMIP particles for CBZ. It can be seen that the kinetic data was better fitted to pseudo-second-order equation than to pseudo-first-order equation according to the correlation coefficient (r^2) (Fig. 4a and Table S2). The result indicates that the adsorption process of CBZ on the MMIP and MNIP adsorbents was predominated by chemical sorption and the sorption capacity is proportional to the number of active sites on the sorbent (Yu, Deng, & Yu, 2008).

In general, the adsorption process on a porous adsorbent may be described as a series of steps: mass transfer from fluid phase to the particle surface across the boundary layer, diffusion within the porous particle, and adsorption itself onto the surface (Pan et al., 2010). Considering the pseudo-second-order model cannot identify

the diffusion mechanism, intraparticle diffusion model was then tested as:

$$Q_t = k_i t^{1/2} \quad (5)$$

where k_i is the intraparticle diffusion rate constant ($\mu mol\, g^{-1}\, min^{-1/2}$). If the intraparticle diffusion is the rate-controlling step, it should be obtained a straight line passing through the origin.

As shown in Fig. 4b, the intraparticle diffusion plots for the MMIP exhibited multi-linearity, indicating that the intraparticle diffusion was not the only rate controlling step, but also other processes might control the rate of sorption. Three steps were involved in the adsorption process for MMIP. The initial stage can be attributed to the boundary layer diffusion of the CBZ from aqueous phase onto the external surface of the MMIP. The second stage described the gradual adsorption of CBZ and the intraparticle diffusion was the rate-limiting step. The last stage was attributed to the final equilibrium where the intraparticle diffusion started to slow down due to the available low CBZ concentrations in the aqueous phase (Pan et al., 2010). This kind of multi-linearity in the shape of the intraparticle diffusion plot was also observed in the adsorption of CBZ onto MNIP.

3.3. Binding isotherms

The binding isotherms of CBZ on the MMIP and MNIP at 25 °C and 35 °C are presented in Fig. 5a. It is clearly demonstrated that the sorption amount of CBZ on to the MMIP and MNIP increased along with the increase of CBZ equilibrium concentration and the temperature had a significant effect on the sorption behavior. The sorption capacity of the MMIP for CBZ was higher than the MNIP, which suggested that the imprinted cavities of the MMIP formed by the imprinting and cross-linking reactions may cause the high affinity binding of the template to the polymer. It is also noted that an increase in the temperature generate an increase in the sorption amount indicating endothermic nature of adsorption process, but the MMIP can get an outstanding adsorption capacity even at the low temperature as shown in Fig. 5a.

Two widely used models including Langmuir equation and Freundlich equation were successfully applied to analyze the sorption data. It is well known that the Langmuir equation has been applied in many monolayer sorption and Freundlich equation is believed to be suitable for describing the adsorption behavior of the non-covalently MIP (Umpleby, Baxter, Bode, et al., 2001; Umpleby, Baxter, Chen, Shah, & Shimizu, 2001; Zhang & Hu, 2008).

As shown in Fig. 5a and Table S3, Freundlich isotherm model fitted the equilibrium data better than that of Langmuir model isotherm. According to the results of Freundlich fitting, all the isotherms are nonlinear because the values of n^{-1} (an indicator of nonlinearity) are in the range from 0.27 to 0.41 ($n^{-1} = 1$ for a linear isotherm). Nonlinearity can be attributed to adsorption site heterogeneity, electrostatic attraction and other sorbent–sorbate interactions (Guo et al., 2011). Moreover, the Freundlich constants (K_F) for CBZ on the MMIP were higher than those on the MNIP, indicating the stronger affinity of the MMIP for CBZ.

In order to further evaluate the specificity, the binding characteristics were discussed using Scatchard plot equation as following:

$$\frac{Q_e}{C_e} = \frac{Q_{max} - Q_e}{K_d} \quad (6)$$

where K_d is the dissociation constant ($\mu mol\, L^{-1}$), Q_{max} is the maximum binding amount ($\mu mol\, g^{-1}$)

As can be seen from Fig. 5b, the Scatchard plot for MMIP is not a single linear curve, but consists of two linear parts with different slopes, indicating that there were two classes of binding sites in the

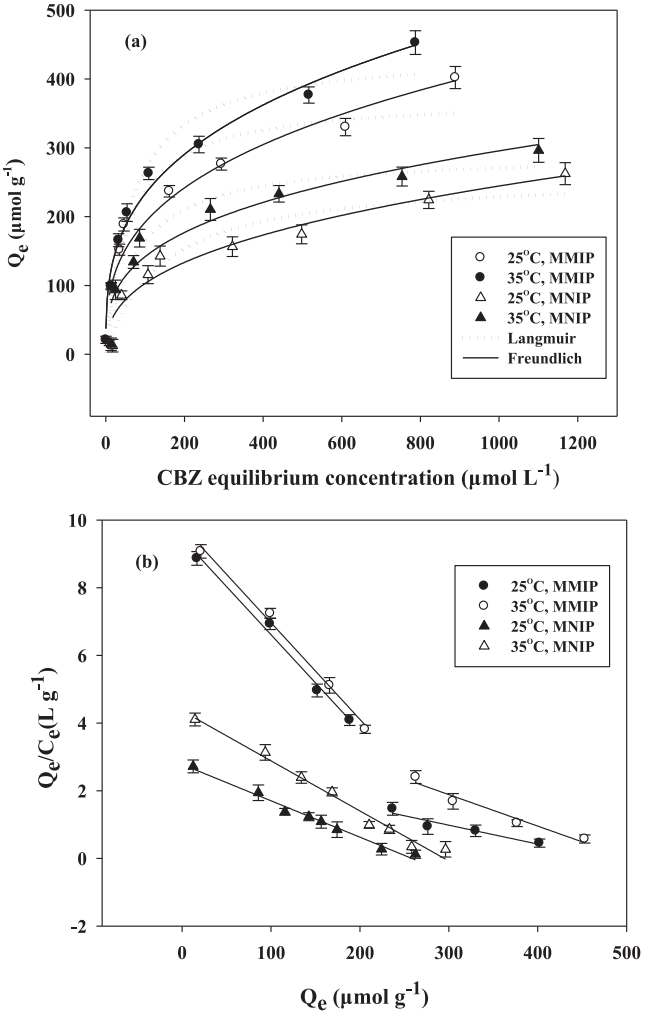

Fig. 5. (a) Adsorption isotherms of the MMIP and MNIP for CBZ in deionized water, and (b) Scatchard plots of the MMIP and MNIP. Adsorbents dose: 10 mg, solution volume: 5 mL,contact time: 2 h.

MMIP and the binding site configuration in the MMIP is heterogeneous (Guo et al., 2011). The binding of CBZ to the MNIP was also analyzed by Scatchard plot. Obviously, it was a single straight line which indicated the binding sites of the MNIP were homogeneous.

3.4. Binding selectivity of MMIP

The binding of MMIP for CBZ was compared to DFC due to their similar chemical structure at a certain extent. As shown in Fig. 6, besides CBZ, quite amount of DFC was adsorbed on MMIP. A comparison of the MMIP binding to MNIP shows that CBZ binding is significantly specific. DFC binding is due to the hydrophobic interaction between the compound and the polymer and hence nonspecific. Therefore, it can be concluded that the MMIP had good binding selectivity in the presence of interferent. Comparatively, the MNIP was affected obviously by the interferent.

3.5. Comparison of removal efficiency using different sorbents

The binding of the MMIP for CBZ in deionized water was compared with that of non magnetic MIP and chitosan. As shown in Fig. 7a, the binding capacity of the MMIP for CBZ was excellent, and the recognition specificity was superior to traditional imprinted sorbents. In addition, MMIP particles possessed of many advantages, such as collected and separation process was more

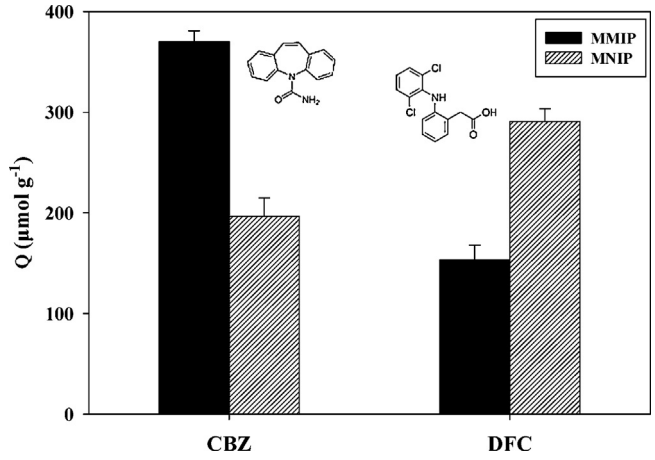

Fig. 6. Binding selectivity of MMIP. Adsorbents dose: 10 mg, initial CBZ and DFC concentration: 100 mg L^{-1}, solution volume: 5 mL, contact time: 2 h.

convenient. Especially, it could be used as intelligent material to respond to magnetic field. The uptake of CBZ onto chitosan probably proves that hydrogen bonding between amino group or carboxyl group in chitosan and amino group in CBZ was involved, and it should play an important role during the MMIP polymerization and eventually lead to the rising adsorption ability of MMIP.

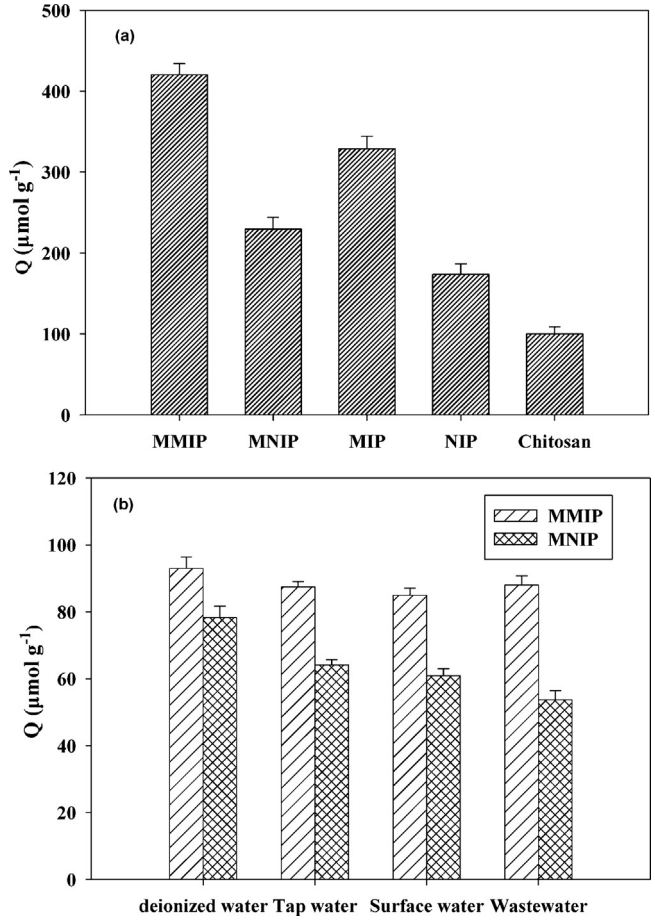

Fig. 7. (a) Sorption of CBZ by different adsorbents and (b) sorption of CBZ from different real water samples. Adsorbents dose: 10 mg, initial CBZ concentration: 50 mg L^{-1}, solution volume: 5 mL, contact time: 2 h.

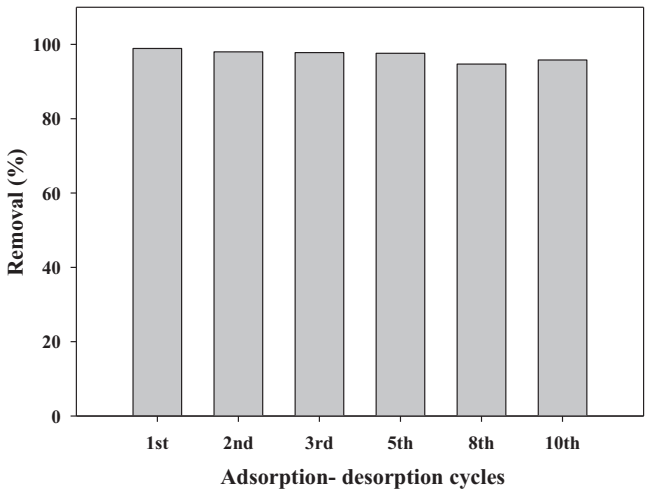

Fig. 8. Reusability of MMIP. Adsorbents dose: 10 mg, initial CBZ concentration: 50 mg L^{-1}, solution volume: 5 mL, contact time: 2 h.

3.6. Removal of CBZ from real water samples

To investigate the potential of MMIP for removing CBZ from complex matrices, spiked deionized water, tap water, surface water and wastewater were applied to MMIP. As shown in Fig. 7b, the sorption amount of MMIP for CBZ in tap water, surface water and wastewater were slightly lower than that obtained in deinoized water, indicating that the capacity of MIP in removing CBZ in real environmental water has been reduced. This is expected due to the presence of many different organic/inorganic contaminants in environmental water bodies which can also bind to MMIP, thus reducing the adsorption capacity of MMIP for CBZ. However, The MMIP binding capacity was still superior to the MNIP. The results suggested the potential application of the MMIP to selectively remove CBZ in water and wastewater.

3.7. Reusability of MMIP

Regeneration experiments were conducted to investigated whether the MMIP can be desorbed/released and reused. After adsorption of CBZ onto the MMIP, the MMIP was regenerated using the methanol/acetic acid (9:1, v:v) and deionized water. Then the regenerated MMIP was reused to adsorb CBZ. Fig. 8 showed the adsorption capacity of the MMIP for CBZ in sorption- desorption cycles. It is seen that the MMIP can be used at least ten cycles without significant loss of adsorption capacity for CBZ, indicating that the MMIP was regenerated during the regeneration process.

4. Conclusions

In this work, CBZ imprinted magnetic polymers based on chitosan-Fe_3O_4 particles were successfully synthesized for selective separation of CBZ from environmental water bodies. This study can be regarded as a combination of selective adsorption and magnetic separation, and the obtained MMIP exhibited higher specific recognition and selectivity to CBZ in the presence of interferent. Although the results reported here relate only to CBZ, the principles of the proposed methodology are expected to be applicable to the removal of other pharmaceuticals from contaminated water. We believe that these surface-imprinted core–shell magnetic beads can be one of the most promising candidates for environmental pollution application.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.05.072.

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