Sonohydrothermal synthesis of MFe_2O_4 magnetic nanoparticles for adsorptive removal of tetracyclines from water

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ABSTRACT

A series of monodisperse magnetic nanoparticles (NPs) MFe_2O_4 ($\text{M} = \text{Fe}^{\text{II}}$, Mn^{II} , Co^{II} , Zn^{II}) was synthesized through an improved sonohydrothermal method and then characterized for their structural properties. NaOH concentration and hydrothermal temperature were examined for their effects on the crystallization of MFe_2O_4 NPs. Thereafter, the synthesized NPs were applied to remove three commonly-used tetracyclines (TCs) from water, including tetracycline (TCN), oxytetracycline (OTC), and chlortetracycline (CTC). High removal efficiencies ($\geq 96\%$) were achieved for all the selected TCs within 5 min. The adsorption kinetics of OTC on MFe_2O_4 NPs could be expressed well by the pseudo-second-order model. Based on the functional groups of TCs and the active surface sites of MFe_2O_4 , the adsorption mechanisms were proposed. The used NPs could be regenerated easily by a methanol solution (60%, v/v) and recycled for the effective removal of TCs. This study demonstrates that the sonohydrothermal method is nontoxic, convenient and cost-effective for the synthesis of magnetic NPs which have potential applications in water treatment for removal of micro-pollutants.

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1. Introduction

Magnetic ferrite MFe_2O_4 (M denotes a divalent metal such as Fe^{II} , Mn^{II} , Co^{II} , Zn^{II}) nanoparticles (NPs) possess special optical, electrical and magnetic properties [1–3], thus have recently attracted much attention in magnetic storage, biosensing, disease diagnosis, catalysis and environmental analysis [4–8]. These applications require that the NPs be monodisperse with small sizes because the physicochemical properties of the NPs strongly depend upon their morphology [9]. However, preventing the aggregation of magnetic NPs so as to obtain suitable particle sizes and a uniform size distribution is always a technical difficulty. Conventional procedures such as the solid-state, hydrothermal and co-precipitation methods are difficult to obtain the uniform MFe_2O_4 NPs [10–12]. To resolve this problem, some new technologies including solvothermal, reverse micelles, and pyrolysis of organometallic compounds have been introduced in the synthesis procedures [13–15], but the use of toxic solvents and/or surfactants, harsh reaction conditions, and expensive raw materials still limit their practical applications. As a result, it is urgent to develop a nontoxic, convenient and cost-effective technique to prepare the MFe_2O_4 NPs.

Antibiotics have been used for many decades as both human and veterinary medicines. In China, the total consumption of antibiotics reached over 120,000 t in 2009 [16]. However, a large portion of antibiotics (about 30–90%) are excreted in urine and faeces without adsorption and metabolism by human or animal bodies [17]. Due to the incomplete removal of antibiotics in wastewater treatment processes as well as the application of composted manure to agricultural farmlands as fertilizer [18], they can eventually reach surface and ground waters [19,20]. Although antibiotics are commonly detected in aquatic environments only at sub-inhibitory concentration levels (from ng/L to $\mu\text{g/L}$), their long-term presence tends to cause a genetic selection of resistant bacteria [21]. Nowadays, serious concerns have been raised regarding the occurrence of antibiotics in the environment and their potential threat to human health and aquatic ecology. Therefore, tetracyclines (TCs), a typical class of antibiotics extensively used worldwide for their broad-spectrum antimicrobial activity against a variety of pathogens, were selected as model pollutants in this work to investigate their adsorptive removal by the synthesized MFe_2O_4 NPs.

This study aimed to develop a new sonohydrothermal method for the synthesis of MFe_2O_4 NPs without organic solvents under mild reaction conditions. The impacts of two important synthesis conditions (i.e., NaOH concentration and hydrothermal temperature) on the crystallization of MFe_2O_4 NPs were examined in detail.

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Afterwards, the synthesized NPs were applied to remove three selected TCs from water. The kinetics and mechanisms of TCs adsorption on MFe_2O_4 NPs were elucidated, and the reusability of the NPs was tested.

2. Experimental

2.1. Chemicals

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 96%), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 98%), manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 98%), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 98%), and zinc chloride (ZnCl_2 , 98%) were purchased from Xilong Chemical Company (Shantou City, China). Sodium hydroxide (98%), sodium perchlorate ($\text{NaClO}_4 \cdot \text{H}_2\text{O}$, 98%), and sodium borate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 96%) were supplied by Sinopharm Chemical Reagent Company (Beijing, China). Acetonitrile and methanol (HPLC grade) were obtained from Fisher Scientific (Houston, TX, USA). The standards of TCs, including tetracycline hydrochloride (TCN, >95%), oxytetracycline hydrochloride (OTC, >95%) and chlortetracycline hydrochloride (CTC, >97%), were purchased from Sigma–Aldrich (St. Louis, MO, USA). The stock solutions of individual TCs were freshly prepared at a concentration of 100 mg/L in ultrapure water produced by a Milli-Q system (Advantage A10, Millipore, Billerica, MA, USA) prior to experiments. The major physicochemical properties of three studied TCs are shown in Table S1.

2.2. Preparation of MFe_2O_4 NPs

Magnetic MFe_2O_4 NPs were prepared by an improved sonohydrothermal method with the following procedures: (1) add a divalent metal (i.e., Fe^{II} , Mn^{II} , Co^{II} , Zn^{II}) salt (0.01 mol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.02 mol) to a glass reactor containing 25 mL of ultrapure water (pre-deaerated with N_2 gas for 15 min), and stir the mixture by using a mechanical agitator at 500 rpm under a gentle N_2 gas stream of 2.5 L/min and a reaction temperature of 30 °C in an ultrasonic device (40 kHz, KQ 300DE, Kunshan, China) until all salts are dissolved; (2) add dropwise NaOH solution (500 mL) with a desired concentration into the reactor, and allow the reactions to proceed for 1 h at 30 °C; (3) transfer the resulting mixture to an autoclave with Teflon lining, heat the autoclave in an oven whose temperature is linearly raised from ambient to a desired hydrothermal temperature at 1–1.5 °C/min, and then hold for 6 h; and (4) apply an external magnetic field (2300 G) to rapidly separate the prepared MFe_2O_4 NPs from the suspension, repeatedly rinse the NPs with a methanol solution (20%, v/v) for three times, and then heat in oven at 65 °C until dry.

The effects of two important synthesis conditions, including NaOH concentration and hydrothermal temperature, on the crystallization of MFe_2O_4 were examined in detail. The NaOH concentration varied from 0.5 to 2.0 M (hydrothermal temperature = 135 °C), and the hydrothermal temperature varied from 95 to 155 °C (NaOH concentration = 1.5 M).

2.3. Characterization of MFe_2O_4 NPs

The crystallite structures of the synthesized MFe_2O_4 NPs were measured by a Bruker D8 Advance X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154056$ nm). Micrographs were obtained from a Hitachi H-7500 transmission electron microscope (TEM) with a field emission gun operating at 200 kV. The elemental composition of the NPs was analyzed by an energy-dispersive X-ray spectroscope (EDS) equipped on a scanning electron microscope (SEM, S-3000 N, Hitachi, Japan). The magnetic properties were

determined by using a vibrating sample magnetometer (VSM, BHV-50HTI, Riken Keiki) with a maximum applied magnetic field of 10 kOe at 300 K. Fourier transform infrared (FTIR) spectra were obtained on a Bruker Tensor 27 spectrophotometer by the KBr pellet technique.

2.4. TCs adsorption on MFe_2O_4 NPs

The adsorptive removal of TCs by MFe_2O_4 NPs was studied via batch experiments. A certain amount of MFe_2O_4 NPs (100 mg) was added to a series of conical glass flasks with each containing 100 mL of TC solution (100 µg/L). Borate buffer was used to maintain the solution pH at 6.9 ± 0.2 . The flasks were placed in an oscillator (HZ-9610 K, Taicang City, China) and shaken in dark at 130 rpm and 15 °C for 12 h. After applying an external magnet (2300 G) close to the glass flask, the supernatant was withdrawn, filtered through 0.22-µm PES syringe filter (Pall, USA), and analyzed for the aqueous concentration of TC. Our preliminary experiment (adsorbent free) had shown that the loss of TCs due to flask wall adsorption and filter interception was less than 5% under the experimental conditions applied.

By taking OTC as example, its adsorption kinetics on MFe_2O_4 NPs was studied. The same experimental conditions, as above mentioned, were adopted except that the ionic strength of the working solution was controlled by 0.05 M NaClO_4 . At preselected time intervals, water samples were taken from the supernatant under an external magnetic field, filtered through 0.22-µm PES syringe filter, and then analyzed for the aqueous concentrations of OTC.

2.5. Regeneration of MFe_2O_4 NPs

After being used for adsorptive removal of TCs from water, the MFe_2O_4 NPs were regenerated by a methanol solution (60%, v/v). Methanol, due to its strong polarity, has been commonly applied to wash off organic adsorbates from the surface of mineral adsorbents. The used MFe_2O_4 NPs were shaken with the methanol solution at 130 rpm and ambient temperature for 30 min. Thereafter, the NPs were separated by an external magnetic field (2300 G), dried in oven at 65 °C for 1 h, and then reused for adsorption of TCs in aqueous solutions. The reusability of the synthesized MFe_2O_4 NPs was tested for nine cycles.

2.6. Analyses of TCs and metal ions

The concentrations of selected TCs were determined by ultra-performance liquid chromatography–tandem mass spectrometry (UPLC-MS/MS, Waters, Milford, MA, US) equipped with a Symmetry C18 column (2.1 mm × 150 mm, 5 µm particle size, Waters). Formic acid (0.2%, v/v) and acetonitrile were used as mobile phases A and B, respectively, with a total flow rate of 0.2 mL/min. The selected TCs were individually analyzed under an isocratic elution condition of 65:35 (A:B, v/v). All the solvents used for UPLC-MS/MS analysis were filtered through 0.22-µm membrane and then degassed by an ultrasonic device for 10 min. The mass spectrometer was operated under the positive electrospray ionization (ESI+) mode and the selected ion recording (SIR) mode was adopted for quantitative analysis of selected TCs. Other MS operation parameters were set according to our previous work [16].

The aqueous concentrations of metal ions (Fe, Mn, Co, and Zn) potentially leached from MFe_2O_4 NPs during the adsorption and regeneration experiments were measured by inductively coupled plasma mass spectrometry (ICP-MS). Results indicate that the leaching of these metal ions was negligible (<10 µg/L) under the applied experimental conditions.

3. Results and discussion

3.1. Characterization of MFe₂O₄ NPs

The XRD patterns of the synthesized MFe₂O₄ NPs are shown in Fig. 1, which matched well with the respective standard cubic spinel structures of Fe₃O₄ (75-0033), MnFe₂O₄ (74-2403), CoFe₂O₄ (22-1086) and ZnFe₂O₄ (89-1010), as indexed by the Joint Committee on Powder Diffraction Standards. The grain sizes of these NPs were calculated by the Debye–Scherrer formula:

$$D_c = K\lambda/\beta \cos \theta \quad (1)$$

where D_c is the grain size (nm), K is Scherrer constant (0.89), λ is the wavelength of the incident X-ray (0.154056 nm), β represents the full width at half maximum of the (311) reflection (rad), and θ represents the diffraction angle of the reflection (°).

The lattice parameters of these NPs were also determined from the cubic phase formula as follows:

$$a = \frac{\lambda}{2} \sqrt{\frac{h^2 + k^2 + l^2}{\sin^2 \theta}} \quad (2)$$

where a is the lattice parameter (nm), and h , k and l are the Miller Bravais indices of the (311) reflection.

The calculated grain sizes of MFe₂O₄ NPs ranged from 28.2 to 56.6 nm with a decreasing order of MnFe₂O₄ > ZnFe₂O₄ > CoFe₂O₄ > Fe₃O₄, which are positively correlated with their lattice parameters and the ionic radii of M^{II} (Table 1). The variation of the lattice oxygen location caused by different ionic radii of M^{II} could significantly affect the grain sizes and the lattice parameter of the NPs [22].

The TEM micrographs clearly show that these magnetic NPs were of cubic shape with a narrow particle size distribution (Fig. 2). It is usually difficult to obtain the magnetic NPs with a regular shape and a narrow particle size distribution only by the hydrothermal method [23], because the magnetic NPs tend to agglomerate to minimize their surface energy. In this study, the introduction of high-frequency ultrasound prior to the hydrothermal process could effectively restrain the agglomeration of the NPs.

The EDS analysis shows that the MFe₂O₄ NPs possessed a homogeneous composition (Fig. S1). The atomic ratio of M:Fe:O was determined to be about 1:2:4 for MnFe₂O₄, CoFe₂O₄ and ZnFe₂O₄, as expected. For Fe₃O₄, the atomic ratio of Fe to O was determined

Table 1

Grain sizes and lattice parameters of MFe₂O₄ NPs prepared at a hydrothermal temperature of 115 °C for 6 h with 1.5 M NaOH.

Properties	Fe ₃ O ₄	MnFe ₂ O ₄	CoFe ₂ O ₄	ZnFe ₂ O ₄
Lattice parameter (Å)	8.35	8.51	8.38	8.44
Grain size (nm)	28.2	56.6	29.8	30.5
Ionic radii (Å)	0.63	0.91	0.82	0.84

as 37:46 since the EDS was not able to differentiate the valences of Fe. This provides further evidence that the synthesized NPs possessed a spinel ferrite structure, which agrees well with the results of XRD analysis.

Field-dependent magnetization of the synthesized MFe₂O₄ NPs was measured at 300 K (±10 kOe). Fig. 3 shows that these NPs had a high magnetism with their saturation magnetization comparable to or even higher than those reported previously [24]. The coercivity measurements show that these NPs (except CoFe₂O₄) had an apparent superparamagnetism, which further proves the nanostructure of these particles. Nanoscale, high saturation magnetization, and superparamagnetism are distinct advantages of the NPs for their applications in biotechnology, medicine and water treatment [11].

The FTIR spectra of the synthesized MFe₂O₄ NPs are shown in Fig. 4a (3000–400 cm^{−1}), with the main infrared absorption peaks and the corresponding assignments interpreted in Table S2. The absorption peaks with a wavenumber larger than 1300 cm^{−1} were generally attributed to the vibrations of –OH (i.e., the –OH stretching vibration (ν_{OH}) and bending vibration (δ_{OH})) and hydrogen bond (or H-bridge). The absorption peaks of MnFe₂O₄ (weak) and ZnFe₂O₄ (strong) near 900 cm^{−1} could correspond to the vibration of M^{II}–O. The peaks at 1061 cm^{−1} for all samples (Fig. 4a) were probably caused by the overtone of the phonons (i.e., $\Delta\nu_L = 2$, $T = 2T_{1u}$) in the 560–600 cm^{−1} region (i.e., 572, 595 and 563 cm^{−1} for MnFe₂O₄, CoFe₂O₄ and ZnFe₂O₄, respectively) (Fig. 4b). It is noted that the characteristic peak of Fe₃O₄ at 590 cm^{−1} partially shifted to 625 cm^{−1} (Fig. 4b), implying the formation of nanoscale particles [25]. The peaks of these NPs observed in the 450–400 cm^{−1} region (e.g., 420 cm^{−1} for CoFe₂O₄) were assigned to the T_{1u} phonon of the Fe–O bond.

3.2. Effect of NaOH concentration

In general, to achieve the crystallization of MFe₂O₄, the final pH of the reaction solution should be controlled above 9.0 by adjusting the alkali concentration [26]. In this study, 500 mL of NaOH solution with various concentrations (0.5, 1.0, 1.5, and 2.0 M) was used to achieve the desired pH condition (i.e., >9.0). Results indicate that the NaOH concentration significantly affected the XRD patterns of ZnFe₂O₄ (Fig. S2a), but had little impact on the XRD patterns of other three MFe₂O₄ NPs (data not shown). As the NaOH concentration was increased to 2.0 M, the diffraction peak of the (311) reflection broadened and the peak intensities of the (400), (422), (511) and (440) reflections weakened. In particular, a new peak emerged at $2\theta = 21^\circ$, which indicates some change of the crystal structure. This is probably attributed to the interactions between the excess OH[−] and the amphoteric Zn(OH)₂ species. However, other alkaline intermediates, including Fe(OH)₂, Mn(OH)₂ and Co(OH)₂, could not react with the excess OH[−]. Thus, NaOH concentration only impacted the crystallization of ZnFe₂O₄.

The grain sizes of ZnFe₂O₄ at different NaOH concentrations could be derived from its XRD patterns using Eq. (1), as provided in Table S3. It is observed that the crystal growth of ZnFe₂O₄ showed special orientation selectivity at different NaOH concentrations, as demonstrated by the different grain sizes along the main reflections (i.e., (311), (220), and (440)).

Fig. 1. XRD patterns of the synthesized MFe₂O₄ NPs. Symbols indicate the expected standard peaks of Fe₃O₄ (□), MnFe₂O₄ (△), CoFe₂O₄ (●), and ZnFe₂O₄ (○).

Fig. 2. TEM micrographs of the synthesized MnFe_2O_4 NPs.

3.3. Effect of hydrothermal temperature

The effect of hydrothermal temperature on the crystallization of the NPs was further investigated by taking the synthesis of ZnFe_2O_4 as example. Results indicate that the peak intensity of the (3 1 1) reflection was enhanced notably with an increasing temperature (Fig. S2b). The grain sizes of ZnFe_2O_4 prepared at different hydrothermal temperatures are shown in Table S3, from which the activation energy of grain growth could be calculated by use of the Coble's formula [27]:

$$\log D_c = -\frac{E_a}{2.303RT} + A \quad (3)$$

where E_a is the activation energy of grain growth (kJ/mol), R is the universal gas constant (8.314 J/mol/K), T is the hydrothermal temperature (K), and A is the pre-exponential factor.

The value of E_a was calculated to be 8.61 kJ/mol (Fig. S3), which is notably lower than that reported by Yang et al. [28] (i.e., 18.5 kJ/mol) who adopted a mechanochemical method to prepare ZnFe_2O_4 . It is seen that the enhanced mass/heat transfer and cavitation induced by ultrasound could effectively reduce the energy barrier of the synthesis process.

3.4. Adsorption of TCs on MnFe_2O_4 NPs

Initial batch experiments show that all the selected TCs could be effectively removed from water (>98.7%) by the synthesized MnFe_2O_4 NPs at a contact time of 12 h (Fig. S4). Taking OTC as example, its adsorption kinetics on different NPs was comparatively examined. Fig. 5 shows that OTC could be rapidly adsorbed on the MnFe_2O_4 NPs. The adsorption kinetics of OTC on the NPs could be fitted well by the pseudo-second-order model [29].

$$\frac{t}{q_t} = \frac{1}{v_o} + \frac{1}{q_e} t \quad (4)$$

where t is the contact time (min), v_o is the initial adsorption rate ($\mu\text{g/g/min}$), and q_t and q_e represent the adsorbed concentrations of OTC ($\mu\text{g/g}$) at time t and equilibrium, respectively. In addition, the initial adsorption rate, v_o , can be directly correlated to q_e , as expressed by the following equation:

$$v_o = k_2 q_e^2 \quad (5)$$

Fig. 3. Room-temperature magnetization curves of the synthesized MnFe_2O_4 NPs.

Fig. 4. FTIR spectra of the synthesized MFe_2O_4 NPs in the wavenumber ranges of $3000\text{--}400\text{ cm}^{-1}$ (a) and $800\text{--}400\text{ cm}^{-1}$ (b).

Fig. 5. Adsorption kinetics of OTC on the synthesized MFe_2O_4 NPs. Experimental conditions: $T = 15^\circ\text{C}$, $\text{pH} = 6.9 \pm 0.2$, $C_{0,\text{OTC}} = 100\text{ }\mu\text{g/L}$, MFe_2O_4 dosage = 1.0 g/L , ionic strength = 0.05 M NaClO_4 . The curves represent the fitting results by the pseudo-second-order model.

where k_2 represents the adsorption rate constant ($\text{g}/\mu\text{g}/\text{min}$).

Results indicate that only after a short contact time of 5 min, 96% of OTC was removed by MnFe_2O_4 and a nearly complete

removal ($>99.5\%$) was achieved by other three NPs (note that the q_t and the removal efficiency are equal in value under the experimental conditions of $C_{0,\text{OTC}} = 100\text{ }\mu\text{g/L}$ and MFe_2O_4 dosage = 1.0 g/L). The simulated kinetic parameters are listed in Table 2. The initial adsorption rates of OTC showed the following order: $\text{CoFe}_2\text{O}_4 > \text{ZnFe}_2\text{O}_4 \approx \text{Fe}_3\text{O}_4 \gg \text{MnFe}_2\text{O}_4$. It is noted that a small difference in the adsorbed concentration of OTC (q_t) between MnFe_2O_4 and other three NPs could lead to a remarkable change of v_0 (Table 2).

The rapid adsorption kinetics manifested that strong affinities existed between the selected TCs and the synthesized MFe_2O_4 NPs. It was reported that hydrogen bonding, surface complexation, and electrostatic force could be the main driving forces for the adsorption of an organic compound on the surface of a metal oxide [30,31]. The FTIR spectra of the synthesized NPs had demonstrated the presence of abundant adsorption sites (e.g., $-\text{OH}$ and $\text{M}^{\text{II}}/\text{Fe}^{\text{III}}-\text{O}$ groups) on the surface of MFe_2O_4 (Fig. 4). According to their pK_a values (Table S1), the selected TCs were mainly present in the aqueous solution as neutral (TC^0) and anionic (TC^-) forms under the experimental pH condition (6.9 ± 0.2). Consequently, hydrogen bonding and surface complexation between the functional groups of TCs and the active surface sites of MFe_2O_4 tended to act as the major driving forces for adsorption.

The FTIR spectra of Fe_3O_4 (before and after adsorption of TCN) and the TCN standard were comparatively examined to clarify the microscopic behaviors of TCN at the liquid–solid interface, as shown in Fig. 6. Results indicate that some new peaks emerged on the surface of Fe_3O_4 NPs after adsorbing TCN. The vibration bands at 2972 , 2925 , 2852 , and 2025 cm^{-1} could be assigned to the stretching vibrations of the hydroxyl ($\nu_{-\text{OH}}$), amine ($\nu_{\text{N}-\text{H}}$), methyl ($\nu_{-\text{CH}_3}$), and carbonyl ($\nu_{\text{C}=\text{O}}$) groups, respectively; other weak peaks in the range from 1600 to 750 cm^{-1} could correspond to the fingerprint peaks of TCN. This result confirms strongly the adsorption of TCN on Fe_3O_4 . It is also noted that most characteristic peaks in the spectrum of the TCN standard showed a certain red shift after being adsorbed on Fe_3O_4 . For example, the standard peak at 2943 cm^{-1} shifted to 2925 cm^{-1} after being adsorbed on Fe_3O_4 , denoting the formation of hydrogen bonding and/or surface complexation between the amide group of TCN and the surface active sites of Fe_3O_4 (e.g., $-\text{OH}$, $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}-\text{O}$). Therefore, the adsorption mechanisms, taking TCN adsorption on Fe_3O_4 as example, are illustrated in Fig. 7.

3.5. Reusability of MFe_2O_4 NPs

The synthesized MFe_2O_4 NPs, after being used for adsorption of selected TCs, were regenerated by simple washing with a 60% (v/v) methanol solution. The regenerated NPs were then applied to remove TCs again. Results indicate that almost all the adsorbed TCs ($>99\%$) could be readily washed off the NPs by the methanol solution, and the regenerated NPs still maintained a high removal efficiency of TCs ($>98\%$) after nine cycles (Fig. S5). Since the synthesized MFe_2O_4 NPs have high adsorptivity for TCs (i.e., $>96\%$ removal within 5 min), fast magnetic separability (i.e., 3 min),

Table 2

Kinetic parameters of the pseudo-second-order model simulation for OTC adsorption on MFe_2O_4 NPs ($T = 15^\circ\text{C}$, $\text{pH} = 6.9 \pm 0.2$, $C_{0,\text{OTC}} = 100\text{ }\mu\text{g/L}$, MFe_2O_4 dosage = 1.0 g/L , ionic strength = 0.05 M NaClO_4).

MFe_2O_4 NPs	v_0 ($\mu\text{g}/\text{g}/\text{min}$)	k_2 ($\text{g}/\mu\text{g}/\text{min}$)	r^2
Fe_3O_4	1196	0.12	0.999
MnFe_2O_4	491	0.05	0.998
CoFe_2O_4	1712	0.17	0.999
ZnFe_2O_4	1323	0.13	0.999

Fig. 6. FTIR spectra of Fe_3O_4 (before and after adsorption of TCN) and the TCN standard.

Fig. 7. Proposed adsorption mechanisms of TCN on Fe_3O_4 : (a) surface complexation between $\text{Fe}^{II/III}$ and the ionic species of TCN and (b) hydrogen bonding between $-\text{OH}$ on Fe_3O_4 surface and the electron-donors ($-\text{OH}/\text{O}^-$, $-\text{NH}_2$) of TCN.

and good reusability, they have potential applications in water treatment for removal of micro-pollutants.

4. Conclusions

- In this study, four monodisperse MFe_2O_4 ($\text{M} = \text{Fe}^{II}$, Mn^{II} , Co^{II} , Zn^{II}) NPs were synthesized through an improved sonochemical method, characterized for their crystal structures and surface properties, and then applied to remove tetracycline antibiotics from water. Based on the obtained results, the following conclusions are drawn:
- The new sonochemical method was nontoxic, convenient and cost-effective for the synthesis of MFe_2O_4 NPs. The grain sizes of the NPs could be controlled well at nanoscale with a uniform distribution.
- NaOH concentration in the studied range of 0.5–2.0 M induced special orientation selectivity of the crystal growth of ZnFe_2O_4 , but had little impact on the crystallization of other three MFe_2O_4 NPs. The application of ultrasound to the hydrothermal method reduced notably the energy barrier of the synthesis process.
- All the selected TCs could be removed by MFe_2O_4 NPs from water effectively and rapidly. Taking OTC as example, its adsorption kinetics was fitted well with the pseudo-second-order model. Hydrogen bonding and surface complexation between the functional groups of TCs and the active surface sites of MFe_2O_4 were the major driving forces for adsorption.
- The used MFe_2O_4 NPs could be regenerated easily by a methanol solution. The regenerated NPs maintained a high efficiency for removal of TCs from water.

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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.seppur.2013.03.046>.

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