Removal of tetracycline antibiotics from aqueous solution by amino-Fe (III) functionalized SBA15

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HIGHLIGHTS

- Amino-Fe (III) functionalized SBA15 was prepared.
- The adsorbent had high adsorption efficiency for all three TCs.
- The differences in the removal trends may be attributed to their pK_a values.
- The complexation of Fe (III) and TCs improved the sorption capacity.

GRAPHICAL ABSTRACT

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ABSTRACT

The gradual increase of antibiotics in aquatic environments poses a serious threat to human health and ecosystems, and removal technology for antibiotics has attracted great interest in recent years. In this study, to improve the adsorption capacity of mesoporous silica, a new sorbent made by grafting both amino groups and Fe (III) on mesoporous silica SBA15 (named Fe-N,N-SBA15) was prepared and used for the removal of tetracycline antibiotics (TCs) from aqueous solution. The results showed that TCs sorption on Fe-N,N-SBA15 was highly pH-dependent, and the optimal pH was found to be 4.5–5.6 for tetracycline (TC), oxytetracycline (OTC) and chlortetracycline (CTC). The adsorption kinetics fitted the pseudo-second-order model perfectly and the adsorption rate constant followed the order OTC > TC > CTC. The adsorption isotherms study showed the maximum sorption capacity to be 143.31, 96.91 and 69.15 mmol kg⁻¹ for OTC, TC and CTC, respectively. The differences in the removal trends of the three TCs may be attributed to their different pK_a values. A thermodynamic study showed that the adsorption of TCs on Fe-N,N-SBA15 is spontaneous ($\Delta G < 0$) and endothermic ($\Delta H > 0$). FTIR and XPS results showed that the high sorption capacity of antibiotics could be mainly attributed to the complexation of Fe (III) and TCs.

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1. Introduction

Antibiotics are widely used as human infectious disease medicines, veterinary medicines and animal husbandry growth promoters [1,2]. However, most of the antibiotics are poorly absorbed and metabolized by humans and animals after intake, so that about 30–90% of administered compounds are released into the environment [3]. In addition, antibiotics are discharged into rivers in the effluents of wastewater treatment plants and feces from animal feeding operations [3–5].

Tetracyclines (TCs), including tetracycline (TC), oxytetracycline (OTC) and chlortetracycline (CTC), constitute one of the most important families of antibiotics. Recently, TCs have been detected in most bodies of water influenced by raw or treated wastewater, including rivers, streams, lakes and ground waters, many of which are used as drinking water sources [6–9]. The increased presence of TCs in the environment raises concerns about their potential to foster the selection of resistant bacteria and resistance genes in the long term as well as serious impacts on the ecosystem [10–12]. As shown in Fig. 1, TCs possess tricarbonylamide, phenolic diketone and dimethylamine groups that confer a marked pH dependent behavior on solubility, and TCs exist as cationic (+00), zwitterionic (± 0), and anionic species ($\pm$ or 0 $-$) under different pH conditions, which introduces more complexity into their behavior in the environment [13]. Consequently, the effective control of the TCs has attracted increasing concern, due to their potential risk and ineffective removal by conventional water treatment. It is of great importance to explore efficient treatment technologies for TCs removal.

Adsorption, due to its simplicity, eco-friendliness and high efficiency, is one of the most important methods for TCs removal [1,14]. Many adsorbents such as soils, montmorillonite, magnetic porous carbon, and surface-functionalized mesoporous silica have been used to adsorb TCs from water [1,13,15,16]. In addition, previous metal–antibiotic interactions studies showed that iron could form stable complexes with TCs. Barbooti et al. found that the ferric ions in clay could form stable complexes with OTC, improving the adsorption characteristics [15]. Özge Hanay et al. proved that increasing iron dose enhanced TC and OTC removal efficiency [17]. Raquel et al. also confirmed that the surface complexation mechanism could be described by the interaction of divalent anion species of OTC with the iron oxide surface [18].

In recent years, ordered mesoporous silica, such as SBA15, has attracted considerable attention from researchers due to its uniform mesoporous structure and high surface area, which can enhance the interaction between the solid surface and guest molecules [19,20]. Furthermore, the pore size of mesoporous silica is large enough to enable facile chemical functionalization of the high density of silanol groups on the pore surface, making mesoporous silica suitable for a wide range of applications in adsorption [20,21]. Among new functionalized mesoporous silica, amino-functionalized silica is very important due to its excellent

chelating ability with heavy metals, but its use as an adsorbent to remove TCs is limited because of the low adsorption capacity.

In this paper, to improve the adsorption of TCs on ordered mesoporous silica, we prepared functionalized SBA15 with both amino groups and Fe (III) (named Fe-N,N-SBA15) for TCs removal. The adsorbent is prepared first by grafting N-(2-aminoethyl)-3-aminopropyltriethoxysilane onto SBA15, followed by the coordination of Fe (III) on the adsorbent. The adsorption behavior and mechanism of TCs onto Fe-N,N-SBA15 were then investigated. The effects of the solution pH and ionic strength on TCs adsorption, adsorption kinetics, adsorption isotherms and thermodynamic parameters were studied. The adsorption mechanism was investigated by Fourier transformed infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Materials and chemicals

Hydrochloride salts of tetracycline, oxytetracycline and chlortetracycline were procured from Sigma Co. and used without further purification. Tetraethyl orthosilicate (TEOS, 98%), Pluronic P123 (PEO₂₀PPO₇₀PEO₂₀, Mav = 5800) and N-(2-aminoethyl)-3-aminopropyltriethoxysilane (96%) was obtained from Alfa Aesar Corp. Acetonitrile and methanol were HPLC grade and obtained from Fisher Scientific Corp. Other chemicals including sodium hydroxide, hydrochloric acid, ferric chloride, isopropanol, and oxalic acid were of analytical grade. All solutions were prepared in high-purity water (Milli-Q).

2.2. Sorbent preparation

Mesoporous silica SBA15 was prepared according to Zhao et al., using TEOS as the silica source and pluronic P123 as the templating reagent [22]. The amino-functionalized SBA15 was prepared in a step-wise fashion using grafting techniques. 3 g of SBA15 was suspended in toluene and an excess amount of N-(2-aminoethyl)-3-aminopropyltriethoxysilane was added drop-wise to the slurry and stirred under reflux at about 100 °C for 24 h. The precipitate was filtered, washed with dry toluene followed by isopropanol and dried overnight, and the product was designated as N,N-SBA15. Incorporation of Fe (III) on the sorbent were carried out by adding 1.5 g N,N-SBA15 to a 0.1 mol L⁻¹ isopropanol solution of ferric chloride and reacted for 24 h. The mixture was filtered, washed with isopropanol and dried overnight. The product was named as Fe-N,N-SBA15. Previous results showed that the amino group and Fe (III) were successfully grafted on SBA15, and that the mesoporous structural order was still maintained after the functionalization. Nitrogen gas sorption isotherms and textural properties were analyzed and the surface area, pore volume and pore size were 245.29 m²/g, 0.38 cm³/g and 6.12 nm. Elemental analysis of

TCs	R ₁	R ₂	pK _{a1}	pK _{a2}	pK _{a3}
TC	H	H	3.30	7.68	9.30
OTC	H	OH	3.27	7.32	9.11
CTC	Cl	H	3.30	7.44	9.27

Fig. 1. Molecular structure and ionization constants of TCs.

Fe-N,N-SBA15 revealed a mass composition of 9.16 wt% C, 2.56 wt% N and 0.27 wt% Fe.

2.3. Characterization techniques

A Tenson 27 FTIR Spectrometer (Bruker, Germany) was used to determine the vibrational frequency changes in the functional groups of virgin and TCs-loaded Fe-N,N-SBA15. The samples of virgin and TCs-loaded adsorbents were mixed with KBr at an approximate ratio of 1/150 (adsorbent/KBr) and then ground in an agate mortar. The resulting mixture was pressed at 10 tons for 2 min to form a pellet, and was then characterized.

Chemical analyses of the virgin and TCs-loaded adsorbents were conducted by XPS (Kratos AXIS ULTRA, UK). The XPS spectra were obtained by applying a monochromatic Al K α (1486.7) X-ray energy source operated at 15 kV and 10 mA. The software package Vision (PR2.1.3) and CasaXPS (2.3.12Dev7) were used to fit the XPS spectra peaks.

2.4. Adsorption batch experiments

All sample tubes or flasks were wrapped in foil to inhibit photo-degradation. For the kinetic adsorption experimental study, 0.5 g Fe-N,N-SBA15 was added into 500 ml solutions in glass flasks containing with each of the TCs at initial concentration 0.1 mmol L⁻¹. The mixed solutions were shaken at a speed of 150 rpm, and hydrochloric acid and sodium hydroxide were used to adjust the solution pH to the desired values. Samples were collected at appropriate time intervals and filtered through a 0.45 μ m membrane filter, and analyzed for the TC concentration.

In the pH effect, ionic strength and adsorption isotherm experiments, polypropylene tubes were used. The pH effect experiments were carried out by adding a mass of 25 mg sorbent into 25 ml solutions containing TCs with the initial concentration of 0.1 mmol L⁻¹. The mixed solutions were shaken at a speed of 150 rpm for 24 h. The solution pH was adjusted to different values between 3 and 9 using hydrochloric acid and sodium hydroxide. After the adsorption, the samples were filtered through a 0.45 μ m membrane filter and analyzed.

For ionic strength experiments, a series of 0.1 mmol L⁻¹ TCs solutions with ionic strength from 0 to 100 mmol L⁻¹ NaCl were prepared. The solution pH was kept at 5.0 $\pm$ 0.1. Other adsorption procedures were the same as those in the above pH effect experiments.

Adsorption isotherm experiments of the TCs were investigated at 298, 308 and 318 K by adding 25 mg adsorbent to 25 ml solutions with initial concentrations of TCs of 0, 0.01, 0.03, 0.05, 0.07, 0.1, 0.15 and 0.2 mmol L⁻¹. The solution pH was kept at 5.0 $\pm$ 0.1. Other experimental conditions were conducted as in the pH effect experiment.

The TC concentrations were determined by HPLC (Agilent 1260, USA) at a wavelength of 360 nm. The mobile phase was a mixture of 10 mmol L⁻¹ oxalic acid–acetonitrile–methanol (67:22:11, v/v) at a flow rate of 1 ml min⁻¹.

Fig. 2. Adsorption kinetics of TCs on Fe-N,N-SBA15. Experimental conditions: [TCs]₀ = 0.1 mmol L⁻¹, m = 1 g L⁻¹, T = 298 K, [NaCl] = 10 mmol L⁻¹, pH = 5.0 $\pm$ 0.1.

3. Results and discussion

3.1. Adsorption kinetics of TCs on Fe-N,N-SBA15

The adsorption kinetics of TCs onto Fe-N,N-SBA15 are shown in Fig. 2. Most TC and OTC were adsorbed rapidly in 100 min, followed by a relatively slow process, and achieved equilibrium with 6 h. CTC was adsorbed quickly in 5 h and achieved equilibrium in 6 h as well. The rapid adsorption observed was probably due to the abundant availability of sorption sites on the surface of the sorbent. The kinetic data were fitted with pseudo-first-order and pseudo-second-order models, which describe mononuclear and binuclear adsorption concerning the adsorbent capacity, respectively [1,23]. The kinetic parameters are listed in Table 1. For all TCs, the pseudo-second-order model fitted better with higher correlation coefficients. The good fit supported the assumption that adsorption of TCs on Fe-N,N-SBA15 was controlled by chemical sorption [24]. The adsorption rate constant k_2 followed the order OTC > TC > CTC, suggesting that OTC was adsorbed onto Fe-N,N-SBA15 more quickly. But comparing the Q_e , the amount of CTC adsorbed was the largest among the three TCs. This was consistent with the sorption of TCs on soil clays, mainly caused by the presence of a chlorine atom in R₁ which could lower the pK_a of the phenolic diketone moiety and increase the water solubility [25]. Compared with TC, CTC and OTC had a chlorine atom and hydroxyl group at R₁ and R₂, respectively, which may affect the properties of TCs and influence their adsorption on the sorbent.

3.2. Effect of pH and ionic strength on the adsorption

Effect of pH and ionic strength on the adsorption of TC onto Fe-N,N-SBA15 are showed in Fig. 3. As listed in Fig. 3(a), the adsorption of TCs onto Fe-N,N-SBA15 was greatly influenced by the solution pH values. The adsorption increased with increasing pH and reached a maximum at approximately pH 5.2, 4.4 and 5.6 for TC, OTC, and CTC, respectively, then decreased with further increase in pH values. The observed results were associated with the characteristics

Table 1

Values of the pseudo-first-order and pseudo-second-order constants of TCs adsorption on the sorbent.

	Pseudo-first-order			Pseudo-second-order		
	Q_e (mmol kg ⁻¹)	k_1 (min ⁻¹)	R^2	Q_e (mmol kg ⁻¹)	k_2 (mmol kg ⁻¹ min ⁻¹)	R^2
TC	13.69	0.006	0.95	18.34	0.0015	0.97
OTC	13.72	0.006	0.96	22.57	0.0022	0.98
CTC	39.95	0.008	0.88	45.45	0.00035	0.90

Fig. 3. Effect of pH (a) and ionic strength (b) on the adsorption of TCs. Experimental conditions: (a) $[TCs]_0 = 0.1 \text{ mmol L}^{-1}$, $T = 298 \text{ K}$, $pH = 3.0 \sim 9.0$, $[NaCl] = 10 \text{ mmol L}^{-1}$; (b) $[TCs]_0 = 0.1 \text{ mmol L}^{-1}$, $T = 298 \text{ K}$, $pH = 5.0 \pm 0.1$, $[NaCl] = 0 \sim 100 \text{ mmol L}^{-1}$.

of the TCs and the adsorbent. Fig. S1 shows that the zero point charge of the Fe-N,N-SBA15 was approximately at pH 8.9. TCs are amphoteric compounds with multiple functional groups, thus may predominantly exist as a cation ($+00$) ($pH < 3.3$), zwitterion (± 0) ($3.3 < pH < 7.6$), and anion ($\pm$ or 0^-) ($pH > 7.6$) (Fig. S2) [13]. In the case of pH below 4.0 and over 9.0, about 20 mmol kg^{-1} of the added TCs were adsorbed due to the unfavorable electrostatic interactions between TCs molecules and adsorbent surfaces, which suggested that surface complexation may be the dominant mechanism for TCs sorption onto the sorbent [18]. As the pH increased from 3.0, the interaction between TCs and sorbent increased mainly attributed to a decrease in TC^{+00} concentration and increase in $TC^{\pm 0}$ concentration. When the pH was in the range of 4.5–6.5, the maximum adsorption of TCs was obtained, mainly caused by surface complexation of $TC^{\pm 0}$, which had its highest concentration in this pH range (Fig. S2). As the concentration of $TC^{\pm}$, TC^{0-} increased at higher pH, a progressive decrease in adsorption was observed which could be attributed to the decreased electrostatic attraction between the negatively charged TCs and the adsorbent. After TCs adsorption, the increasing negative charge of the sorbent surface suggested that the interaction between TCs and adsorbent was mainly caused by surface complexation [26,27]. The small differences in the removal trends of three TCs at different pH may be attributed to their pK_a values as influenced by the characteristics of the chemical groups at the R_1 and R_2 positions of the TC molecules (Fig. 1).

Fig. 3(b) shows that the concentration of NaCl had little effect on the adsorption of TCs on Fe-N,N-SBA15 when ionic strength increased from 0 to 100 mmol L^{-1} . It has been reported that inner-sphere complexes are hardly influenced by changes in ionic strength, where outer-sphere complexes are greatly influenced [28,29]. Hence, the adsorption of TCs on Fe-N,N-SBA15 may be related to the formation of inner-sphere surface complexes between adsorbate and adsorbent, consistent with the report by Gu et al. that TC forms inner-sphere complexes with both Fe and Al hydrous oxides [2].

3.3. Adsorption isotherms

The adsorption isotherm is critically important in designing an adsorption system. Adsorption isotherms of TCs onto Fe-N,N-SBA15 at pH 5.0 are plotted in Fig. 4. The sorption data were fitted by the Langmuir and Freundlich equations [23], and the calculated parameters are summarized in Table 2. It was found that the

Fig. 4. Adsorption isotherms of TCs on Fe-N,N-SBA15. Experimental conditions: $[TCs]_0 = 0 \sim 0.2 \text{ mmol L}^{-1}$, $m = 1 \text{ g L}^{-1}$, $T = 298 \text{ K}$, $pH = 5.0 \pm 0.1$, $[NaCl] = 10 \text{ mmol L}^{-1}$.

Langmuir model provided a better fit to the observed data for the TCs, with high correlation coefficients ($R^2 = 0.98$). The maximum OTC, TC and CTC sorption capacities ($Q_{\max}$) were 143.31, 96.91 and $69.15 \text{ mmol kg}^{-1}$, respectively. The values of $1/n$ were less than 1.0 for all TCs, suggesting that the adsorbent was favorable for the removal of TCs from aqueous solution [23].

It was reported that the sorption capacity of TCs on magnetic porous carbon, microscale zerovalent iron, cross-linked chitosan and hydrophilic molecularly imprinted polymers were 53 mmol kg^{-1} [1], 49 mmol kg^{-1} [17], 43 mmol kg^{-1} [30], and $23\text{--}54 \text{ mmol kg}^{-1}$, respectively [24]. The current results clearly indicate that the Fe-N,N-SBA15 sorbent developed in this study has great potential for removal of antibiotics from aqueous environments.

Table 2

Langmuir and Freundlich parameters for the adsorption of TCs on Fe-N,N-SBA15.

	Langmuir			Freundlich		
	$Q_{\max} (\text{mmol kg}^{-1})$	$b (\text{L mg}^{-1})$	R^2	n	K_f	R^2
TC	96.91	0.067	0.98	1.51	271.77	0.93
OTC	143.31	0.088	0.98	1.31	478.01	0.97
CTC	69.15	0.015	0.98	2.17	195.35	0.89

Table 3

Thermodynamic parameters for the adsorption of TC onto Fe-N,N-SBA15.

	Temperature (K)	K_c (L g ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	R^2
TC	298	0.51	1.53	35.77	0.11	0.99
	308	0.87	0.39			
	318	1.26	-0.76			
OTC	298	1.11	-0.15	43.42	0.14	0.97
	308	1.71	-1.61			
	318	3.35	-3.07			
CTC	298	1.56	-0.73	46.75	0.16	0.92
	308	1.80	-2.32			
	318	5.10	-3.91			

3.4. Adsorption thermodynamics

To study the adsorption of TCs on Fe-N,N-SBA15 further, the temperature effect on the adsorption process is investigated and the thermodynamic parameters such as the Gibbs free energy (ΔG°), the enthalpy (ΔH°), and the entropy (ΔS°) were calculated [1]. Qualitative estimates of ΔH° and ΔS° can be obtained from the slope and intercept of $\ln K_d$ vs $1/T$ as shown in Fig. S3. The resulting thermodynamic parameters are presented in Table 3. The positive values of ΔH° (35.77, 43.42, and 46.57 kJ mol⁻¹) for the TCs indicated the endothermic nature of the overall adsorption process. As ΔH° was in the range of 30–70 kJ mol⁻¹, the adsorption of TCs on the sorbent was considered to be chemisorption [16]. The endothermic characteristic revealed that the adsorption process was more favorable at higher temperature. The positive values of ΔS° were consistent with the fact that the adsorption process was irreversible and favored sorption. The spontaneity of the adsorption process was illustrated by the negative values of ΔG° . Furthermore, the value of ΔG° decreased with increasing temperature, indicating that the reaction between TCs and adsorbent was more favorable at higher temperatures. The results were consistent with those for the adsorption of TC on magnetic porous carbon [1].

3.5. Adsorption mechanism

To further investigate the adsorption mechanism of TCs on Fe-N,N-SBA15, the FTIR and XPS data for the adsorbents before and after the adsorption of TCs were analyzed.

FTIR spectra of the adsorbents are shown in Fig. 5. Since the most characteristic region of the TCs spectrum occurred between 1400 and 1700 cm⁻¹, only this region was interpreted in detail. As the spectra of TC, OTC and CTC had no differences, only the FTIR spectra of TC are shown.

Peak assignments for TC (Fig. 5a) followed the study of Gu et al. and Chang et al. [2,31]. The 1672 and 1523 cm⁻¹ bands were assigned to the carbonyl and amino groups of the amide in ring A, respectively. The frequencies at 1614 and 1581 cm⁻¹ correspond

Fig. 5. FTIR spectrum of the virgin and TCs-loaded sorbents. (a) TC; (b) CTC-loaded sorbent; (c) OTC-loaded sorbent; (d) TC-loaded sorbent; (e) Fe-N,N-SBA15.

to the carbonyl groups in A and C rings or the amid-NH, and the 1455 cm⁻¹ band was assigned to the C=C skeletal vibration. The spectra of the three TCs equilibrated with Fe-N,N-SBA15 were similar (Fig. 5b–d), indicating similar adsorption mechanisms for the molecules. The band at 1672 cm⁻¹ for TC shifted to a lower frequency, and a decrease in the relative peak intensity of the 1523 cm⁻¹ band showed that the carbonyl and amino group of the amide in ring A may have reacted with Fe (III) on the sorbent. The band at 1614 cm⁻¹ shifted to a higher frequency, indicating that the carbonyl groups or the amid-NH in ring A may have been influenced by the complexation of TCs and Fe (III) on the sorbent. This was consistent with the complexation of TC and hydrous oxides of Al, Fe [2,31]. The intensity of the 1581 cm⁻¹ band decreased, and the slight shift of the 1455 cm⁻¹ band indicated that carbonyl groups of ring C or amid-NH in ring A of the TCs may form complexes with Fe (III) on the sorbent.

Fig. 6. The XPS spectrum of C 1s and N 1s on the virgin and TCs-loaded sorbents. (a) Fe-N, N-SBA15; (b) TC-loaded sorbent; (c) OTC-loaded sorbent; (d) CTC-loaded sorbent.

The high-resolution C 1s and N 1s XPS spectra of the sorbents before and after adsorption of TCs are shown in Fig. 6. The C 1s spectra could be divided into three individual component peaks: 287.9–288.2 eV was attributed to C=O or O–C–O, 286.2–286.4 eV was associated with C–(O, N), and 284.8 eV was assigned to C–(C, H). A comparison between sorbents before and after the reaction with TCs showed that the binding energy of C–(C, H) peaks had no changes, a slight rise of binding energy was observed at C–(O, N) from 286.2 eV to 286.4 eV, and C=O or O–C–O from 287.9 eV to 288.2 eV. These shifts indicated that the electron distribution in the sorbent was disturbed, as evidenced by the increases in the electronic density around C in C–(O, N) and C=O. The relative content of C–(C, H) was observed to increase from 49% to 54%, while C–(O, N) decreased from 46% to 39% (Table S1). These results may be attributed to the interaction between Fe (III) of the sorbent and amide of TCs.

N 1s spectra exhibited two peaks: 399.5 eV was assigned to the amino group, and the peak at 401.0 eV was attributed to amino perturbed by Fe (III), which was also reported by Chen et al. and Zuo et al. [32,33]. After TC adsorption, the binding energy of 401.0 eV decreased to 400.5 eV, and the relative content increased from 44% to 61%, 53%, 52% for TC, OTC and CTC, respectively (Table S1). This may be caused by interaction between the Fe (III) on the sorbent and the amino group of TCs. The amino group of TCs could form a Fe–N covalent bond by donating a lone pair of electrons, causing an increase in the electron cloud density and lower binding energy of NH–Fe on the sorbent. The results were consistent with those observed in the formation of Copper–N bonding [34]. Because the new NH–Fe (III) bond formed, the relative content of the 401.0 eV peak increased.

4. Conclusions

This article offered a new sorbent for the removal of TCs from aqueous solution. Due to the complexation interaction between Fe (III) and TCs, the TCs were adsorbed on Fe–N,N-SBA15. The pH influenced the adsorption of TCs significantly and the most effective pH was approximately 4.4–5.6. The adsorption of TCs on Fe–N,N-SBA15 was fast and the isotherms were fitted with the Langmuir model perfectly. The thermodynamic parameters derived from the results showed that the adsorption process of TCs is spontaneous and endothermic. The differences in the constituent groups of the TCs induced slight changes in adsorption on the sorbent. All the results showed that the sorbent Fe–N,N-SBA15 showed excellent adsorption behavior for TCs and could be used as a potential sorbent for the removal of antibiotics.

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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.colsurfa.2015.02.018>.

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