Preparation of amino-Fe(III) functionalized mesoporous silica for synergistic adsorption of tetracycline and copper

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HIGHLIGHTS

- A novel adsorbent contained amino groups and coordinated Fe(III) was prepared.
- The adsorbent had high adsorption efficiency for both TC and Cu(II).
- The synergistic effects of TC and Cu(II) on the adsorption were found.
- TC–Cu(II) complex act as a bridge between adsorbates and adsorbent.
- Fe(III) and amino groups were complexed with amide of TC and Cu(II), respectively.

GRAPHICAL ABSTRACT

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ABSTRACT

Finding effective methods for simultaneous removal of antibiotics and heavy metals has attracted increasing concern since both of them are frequently detected in aquatic environments. In this study, a novel mesoporous silica adsorbent (Fe-N,N-SBA15) contained dual-functional groups was synthesized by first grafting di-amino groups on SBA15, and then coordinating Fe(III) onto the adsorbent. The adsorbent was then used in the synchronous elimination of tetracycline (TC) and Cu(II) from water, which was deeply studied by solution pH, kinetics, equilibriums in sole and binary systems. It was found that the adsorbent had high affinity for both TC and Cu(II) and synergistic effects on the adsorption were found. The solution pH remarkably affected the adsorption due to pH-dependent speciation of TC, Cu(II), TC–Cu(II) complex and the surface properties of the adsorbent. Increasing adsorption amount of TC and Cu(II) on the adsorbent could be attributed to the formation of complex TC–Cu(II) bridging or the stronger affinity of the adsorbent for the TC–Cu(II) complex than that for TC or Cu(II) separately. FT-IR and XPS studies revealed that Fe(III) and amino groups on the adsorbent were complexed with the amide of TC and Cu(II), respectively. The recyclabilities of the adsorbent were also evaluated and the Fe-N,N-SBA15 exhibited good reusability for TC and Cu(II) removal. This study shows guidelines and offers an innovative, effective method for the synergistic removal of antibiotics and heavy metals from aquatic environments.

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1. Introduction

In recent years, combined pollution of antibiotics and heavy metal ions has been an increasingly concern in aqueous solution

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due to it reflects the real environment. Antibiotics have been heavily used as a feed additive to treat disease and promote the growth of animals (Polubeshova et al., 2006). While antibiotics are poorly absorbed in the digestive tract of animals, and 50–80% of them are excreted into environment as parent compounds (Sarmah et al., 2006). Heavy metals, which are mostly acute toxic to human and wildlife even in trace level, are widely used as a growth promoter in many animal feeds and in industrial, resulting in high concentrations in some animal wastes and wastewater (Xiong et al., 2010; Yang and Jiang, 2014). The application of animal wastes and wastewater has increased their concentrations in the aquatic environments. Both antibiotics and heavy metals are frequently detected simultaneously in ground water and surface water (Kolpin et al., 2002; Li and Zhang, 2013; Lindsey et al., 2001; Luo et al., 2011; Satapathy et al., 2009). Antibiotics can combine with heavy metals strongly and produce complex species, which makes the behaviors of both compounds more complicated. Furthermore, growing evidence suggests that the toxicity of complex species is generally larger than their individual toxicity (Lian et al., 2013). Consequently, the need for effective elimination methods for antibiotics and heavy metals pollution from aqueous solution has attracted increasing concern.

A variety of treatment methods has been established for the removal of antibiotics and heavy metals from water (Farooq et al., 2002; Le-Minh et al., 2010; Lopez et al., 2003; Zazouli et al., 2009; Zhao et al., 2010). Among these methods, adsorption remains attractive because of its advantages of easy operation, energy savings and high removal capacity. Many adsorbents have been used to adsorb antibiotics or heavy metals from water separately, but fewer were used to remove them together (Figueroa et al., 2004; Ge et al., 2012; Ji et al., 2009; Oh et al., 2007; Sassman and Lee, 2005; Vu et al., 2010; Yang and Jiang, 2014; Hasan et al., 2013). In recent years, the cosorption of antibiotics and heavy metals from water by some adsorbents has been attracting increasing concern due to the realistic demands (Kang et al., 2010; Ling et al., 2013; Wang et al., 2008). Sometimes antagonistic effects on adsorption were found when they coexist. So it is of significance to explore new adsorbents for synergistic removing antibiotics and heavy metals simultaneously from water. Furthermore, as the structure of an adsorbent plays an important role on its properties, investigating the roles of functional groups and interaction processes of simultaneously removal antibiotics and heavy metals can provide more guidelines for operation of water treatment.

Mesoporous silica material has been the focus of explosive interest because of its fascinating characteristics of large surface area, tunable pore structure and well-understood surface chemistry (Bui and Choi, 2009). In order to increase the adsorption capacity of emerging contaminants, surface-modified SBA15 with functional groups has been used as adsorbent for the removal of pollutants from aqueous solution (Bui et al., 2011, 2013; Wu et al., 2013). Amino-functionalized SBA15 has proved to be one of the most useful sorbents for removing heavy metals from water due to its excellent chelating ability (Aguado et al., 2009). Metal grafting SBA15 shows high adsorption capacity in the removal of pharmaceutical drugs for water treatment (Rivera-Jimenez and Hernandez-Maldonado, 2008; Rivera-Jimenez et al., 2010). In connection with the ability of Fe(III) to form stable complexes with antibiotics (Barbooti et al., 2014), we proposed an adsorbent with dual functionalization of amino groups and Fe(III) based on SBA15, for synergistic removal of antibiotics and heavy metals, whereas few studies have thoroughly discussed.

The purpose of this work is to preparing a novel adsorbent for removal antibiotics and heavy metals simultaneously. Using SBA15 as support, di-amino groups was first grafted on and then Fe(III) was complexed with the amino groups, and the adsorbent

was designated as Fe-N,N-SBA15. The structure, textural, and morphological properties of the adsorbent were characterized. Due to the high complexation between antibiotics, heavy metals and Fe(III), amino group, respectively. The adsorption and cosorption of TC and copper on Fe-N,N-SBA15 was systematically investigated because of their great production and consumption in China. Roles of amino and Fe(III) groups of the sorbent and interaction processes of TC and copper were investigated by studying pH, kinetic and adsorption isotherms in sole and binary systems. In addition, the adsorption mechanisms were elucidated based on the results of Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS).

2. Experimental section

2.1. Reagents and materials

SBA15 was obtained from Nanjing XFNANO Materials Tech Co., Ltd. N-(2-aminoethyl)-3-aminopropyltriethoxysilane (96%) was obtained from Alfa. Tetracycline (96% purity) was obtained from Beijing Jing Ke Hong Da Biotechnology Co., Ltd., and used without further purification. Toluene, acetonitrile, methanol, and isopropanol were HPLC grade and obtained from Fisher Scientific Corp. Other chemicals, including sodium hydroxide, hydrochloric acid, ferric chloride, copper chloride, and oxalic acid were analytical grade. Ultrapure water was used for all experiments.

2.2. Preparation of Fe-N,N-SBA15

The amino-functionalized SBA15 was synthesized in post-synthesis grafting method. For the chemical incorporation of amino-organic moieties, 3 g of SBA15 was pretreated at 120 °C for 2 h in a nitrogen atmosphere to remove water. Then the solid was suspended in toluene and stirred for approximately 1 h. 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 N,N-SBA15. Incorporation of Fe(III) into N,N-SBA15 was carried out by the reaction of N,N-SBA15 with a 0.1 M isopropanol solution of ferric chloride for 24 h at 25 °C. The mixture was then filtered, washed with isopropanol and water. Finally the obtained product was air-dried for 12 h, and further dried at 80 °C overnight named as Fe-N,N-SBA15.

2.3. Adsorbents characterization

X-ray powder diffraction (XRD) patterns were obtained using an X'pert PRO MPD (PANalytical, Holland). All XRD patterns were collected in the 2θ range between 0.5° and 3° with a scanning rate of 0.01°/min. The textural properties of the samples were measured via nitrogen adsorption isotherms recorded by a Micromeritics ASAP 2020 HD88 (Mike, USA). The total surface area, pore volume and pore size distribution (PSD) of the samples were calculated with built-in software. PSD were calculated from the desorption branch of the N₂ isotherm data using the Barret–Joyner–Halenda (BJH) method. A Tenson 27 FTIR Spectrometer (Bruker, Germany) was used to determine the vibration frequency changes for the functional groups of virgin and adsorbate-loaded Fe-N,N-SBA15. The chemical analyses on the virgin and TC/Cu(II) loaded Fe-N,N-SBA15 were conducted by XPS (Kratos AXIS ULTRA, UK). The XPS spectra were obtained by applying a monochromatic Al K α (1486.7 eV) X-ray energy source operated at 15 kV and 10 mA. The software packages Vision (PR2.1.3) and CasaXPS (2.3.12Dev7) were used to fit the XPS peaks.

2.4. Adsorption experiments

All experiments were conducted at $25 \pm 1^\circ\text{C}$ with an ionic strength of 10 mM NaCl and all solutions were wrapped with aluminum foil to prevent light-induced decomposition of TC. In this study, all the experiments were performed in triplicate, and the values listed in the figures were calculated by the average. In the kinetic experiments, three sets of 500 mL solutions with TC concentration of 0.1 mM, Cu(II) concentration of 0.25 mM, and simultaneous TC concentration of 0.1 mM and Cu(II) concentration of 0.25 mM, were prepared respectively. The adsorbent was then added into the solution with a dosage of 1 g L^{-1} . The mixed solution was shaken with a speed of 150 rpm in darkness. HCl and NaOH solutions with the concentration of 0.1 M were used to adjust the pH to 5.5 ± 0.1 . The samples were collected at appropriate time intervals, filtered through a $0.45\text{ }\mu\text{m}$ membrane filter and the concentrations of the TC and Cu(II) were analyzed.

The effect of pH on the simultaneous adsorption of TC and Cu(II) on Fe-N,N-SBA15 was investigated as follows. First, four sets of 25 mL solutions were prepared. One set of solutions contained TC concentration of 0.1 mM, and the second set of solutions contained Cu(II) concentration of 0.25 mM. The third set of solutions contained TC concentration of 0.1 mM and Cu(II) concentration of 0.25 mM. The fourth set of solutions contained TC concentration of 0.1 mM and Cu(II) of 0.5 mM. Fe-N,N-SBA15 was added into each solution with a dosage of 1 g L^{-1} and the mixed solution was shaken with a speed of 150 rpm for 24 h. The solution pH was kept at desired values in the range of 3.0–9.0 using HCl and NaOH during the adsorption process. Finally, the solutions were filtered and the concentrations of TC and Cu(II) were analyzed.

Adsorption isotherms of TC with or without Cu(II) were studied as follows. A series of 25 mL solutions with TC concentrations of 0–0.25 mM, with or without 0.25 or 0.5 mM Cu(II) were prepared. For the adsorption isotherms of Cu(II) with or without TC, the initial concentrations of Cu(II) were 0–2.5 mM, and TC concentrations of 0 or 0.1 mM. The adsorbent was then added into the solutions with a dosage of 1 g L^{-1} and the solution pH was kept at 5.5 ± 0.1 . Other experimental conditions were the same as the pH effect experiments.

The regeneration of adsorbent was carried out by desorbing TC/Cu with 0.1 mM HCl aqueous solution. After being filtered and washed with ultrapure water, the sorbent were air-dried for 12 h, and further dried at 80°C overnight. The amount of residual TC/Cu(II), Fe(III) and N atoms on the adsorbent were analyzed.

The TC concentrations were determined by HPLC (Agilent 1260, USA) at a wavelength of 360 nm. The mobile phase was a mixture of 10 mM aqueous oxalic acid-acetonitrile-methanol (67:22:11, v/v) at a flow rate of 1 mL min^{-1} . The Cu(II) concentrations were determined by inductively coupled plasma optical emission spectrometer (ICP-OES) (Elan 5000, Perkin Elmer, USA).

3. Results and discussion

3.1. Structure, textural, and morphological properties of Fe-N,N-SBA15

The low-angle X-ray powder diffraction data of sorbents are displayed in Fig. 1a. SBA15 exhibited three well-defined diffraction peaks in the range of $0.8\text{--}2^\circ$, which could be indexed to the (100), (110), (200) planes of the porous structure, suggesting a $p6mm$ symmetry-typical of uniform mesopore structures with hexagonal long-range order (Zhao et al., 1998). Compared with unmodified SBA15, d_{100} , d_{110} and d_{200} were still present for N,N-SBA15, demonstrating that the structure of SBA15 was maintained after the modification. However, the reduction in diffraction intensity revealed some extent of disorder, especially for the d_{110} and d_{200} peaks, which indicated that the amino group had been successfully grafted to SBA15 (Aguado et al., 2009). After coordinated with Fe(III), the diffraction of the d_{110} and d_{200} peaks nearly disappear, suggesting that the metal modification reduced the scattering power of SBA15 due to the incorporation of metal (Rivera-Jimenez et al., 2010).

SBA15 exhibited the highest surface area, while the loading of amino groups and Fe(III) resulted in a decrease in the value, following the order SBA15 ($499\text{ m}^2\text{ g}^{-1}$) > N,N-SBA15 ($296\text{ m}^2\text{ g}^{-1}$) > Fe-N,N-SBA15 ($249\text{ m}^2\text{ g}^{-1}$). The same phenomenon was found with pore volume, decreasing from $0.89\text{ cm}^3\text{ g}^{-1}$ of SBA15 to $0.49\text{ cm}^3\text{ g}^{-1}$ of Fe-N,N-SBA15 (Table S1). These observations also confirmed the successful loading of functional groups on the surface of SBA15. The FT-IR spectra of the adsorbents (Fig. S1) also confirmed the modification of SBA15 by amino-groups and metals. After modification the isotherms of N,N-SBA15 and Fe-N,N-SBA15 were of type IV with H2 hysteresis loops, which was typical of SBA15 materials (Fig. 1b). Although the hysteresis shifted to lower relative pressures, a comparison of the PSD curves for adsorbents revealed that the grafting method did not have much influence on the average pore size (Fig. 1b). These observations were in agreement with the low-angle XRD patterns findings, suggesting

Fig. 1. Characterization of studied samples by: (a) XRD; (b) N_2 adsorption/desorption isotherms and inset with PSD curve.

that the adsorbents preserved the mesoporous structural order after the functionalization of the amino/metal groups.

3.2. Adsorption kinetics

The adsorption and cosorption kinetics of TC and Cu(II) onto Fe-N,N-SBA15 are shown in Fig. 2. For the sole system, TC or Cu(II) was adsorbed rapidly in the first 30 min, and followed by a relatively slow process. The rapid adsorption rate could be attributed to the rigid, open-pore structure as well as the large pore size of adsorbent, which increased the internal mass transfer in the adsorption process. Furthermore, the protonated amino group and Fe(III) inside the pore walls could provide abundant binding sites for Cu(II) and TC, respectively (Barbooti et al., 2014; Yang and Jiang, 2014). For the binary system, the presence of Cu(II) increased the adsorption rate of TC and enhanced the amount of adsorbed TC to more than twice values in the absence of Cu(II) (Fig. 2a). As shown in Fig. 2b, the presence of TC also facilitated the adsorption of Cu(II). TC and Cu(II) could facilitate the

adsorption of one another, which might be attributed to the strong chelating capability of TC and Cu(II). The Cu(II) and TC, which adsorbed on different sites of Fe-N,N-SBA15, could chelate the TC and Cu(II) in the solution by formation of TC–Cu(II) complexes with higher sorption affinity (Ling et al., 2013).

3.3. Effect of pH on adsorption and cosorption of TC and Cu(II)

Fig. 3a shows that solution pH remarkably affected TC adsorption on Fe-N,N-SBA15, and the presence of Cu(II) can increase TC adsorption significantly. In the absence or presence of 0.25 mM Cu(II), the adsorption of TC increases to a maximum and then decreases with increasing solution pH. In the presence of 0.5 mM Cu(II), the adsorption of TC increases when the solution pH is increased from 3.1 to 6.0 and then remains unchanged with the solution pH increased further. As displayed in Fig. 3b, the Cu(II) adsorption on Fe-N,N-SBA15 with and without TC increases with the solution pH increases up to 5.5, then it remains unchanged as the solution pH is further increased to 9.0. It also can be seen

Fig. 2. Adsorption kinetics of TC and Cu(II) onto Fe-N,N-SBA15. (a) TC adsorption in the absence or presence of Cu(II). Experimental conditions: $[TC]_0 = 0.1$ mM, $[Cu(II)]_0 = 0$ or 0.25 mM, $m = 1$ g L⁻¹, pH = 5.5 ± 0.1, $T = 25$ °C. (b) Cu(II) adsorption in the absence or presence of TC. Experimental conditions: $[Cu(II)]_0 = 0.25$ mM, $[TC]_0 = 0$ or 0.1 mM, $m = 1$ g L⁻¹, pH = 5.5 ± 0.1, $T = 25$ °C.

Fig. 3. Effect of pH on adsorption of TC and Cu(II). (a) Effect of pH on TC adsorption in the absence or presence of Cu(II). Experimental conditions: $[TC]_0 = 0.1$ mM, $[Cu(II)]_0 = 0$, 0.25 or 0.5 mM, $m = 1$ g L⁻¹, $T = 25$ °C. (b) Effect of pH on Cu(II) adsorption in the absence or presence of TC. Experimental conditions: $[Cu(II)]_0 = 0.25$ mM, $[TC]_0 = 0$ or 0.1 mM, $m = 1$ g L⁻¹, $T = 25$ °C.

that the presence of TC increases the adsorption amount of Cu(II) on the adsorbent.

The results showed above can be associated with the pH-dependent speciation of TC, Cu(II), the complex of TC–Cu(II) and the surface properties of the adsorbent. Results of zeta potential measurements of the adsorbent indicated that the surface of Fe–N,N-SBA15 was positively charged over the studied pH range (Fig. S2). TC (symbolized as H_2L) is an amphoteric molecule and formed a series of species at different pH levels, the distribution of various species was calculated by MINEQL⁺ (Kang et al., 2010). The predominant TC species were H_3L^+ at $pH < 3.4$, H_2L at $3.4 < pH < 7.6$, HL^- at $7.6 < pH < 9.0$, and L^{2-} at $pH > 9.0$ (Fig. S3). With pH increasing from 3.0 to 5.5, the percentage of the neutral form (H_2L) increased and the amino group on TC was more easily complexed with Fe(III) on the adsorbent due to the electrostatic attractions, which increased the amount of adsorption (Lian et al., 2013). With the pH further increasing, the percentage of anionic form (HL^- , L^{2-}) increased, which inhibits the adsorption of TC on Fe–N,N-SBA15 due to the electrostatic repulsion. The adsorbent contains amino groups, which have a strong complexing capability with Cu(II). With increasing pH, the positive charge of the adsorbent decreases (Fig. S2), due to the increasing electrostatic attraction, the adsorption amount of Cu(II) is enhanced.

When TC and Cu(II) were present in the solution simultaneously, the strong chelating capability between TC and Cu(II) resulted in complex species. The distribution of TC–Cu(II) species was determined by the MINQL⁺ including $Cu(H_2L)^{2+}$, $Cu(HL)^+$, $Cu(L)$, $Cu(H_4L_2)^{2+}$, $(CuH_3L_2)^+$, (CuH_2L_2) , $(CuHL_2)^-$ (Fig. S3) (Kang et al., 2010). The synergistic effect of TC and Cu(II) adsorption might be ascribed to the strong complex formation between TC and Cu(II). The Cu(II) or TC could act as a bridge between the adsorbate and Fe–N,N-SBA15. Furthermore, the complex of TC–Cu(II) may have stronger affinity to the adsorbent than TC and Cu(II) separately. A similar observation was reported on the adsorption of TC on waste tire powder and montmorillonite (Lian et al., 2013; Wang et al., 2008).

3.4. Adsorption isotherms

Adsorption isotherms of TC on Fe–N,N-SBA15 at pH 5.5 with and without Cu(II) are shown in Fig. 4a. The amount of TC adsorbed on Fe–N,N-SBA15 increased with increasing TC equilibrium

concentration. The adsorption amount of TC was significantly enhanced with the increasing concentration of Cu(II). The same phenomena was reported for the adsorption of TC onto chelating resin and tire powder (Lian et al., 2013; Ling et al., 2013). Lian et al. confirmed that TC and Cu(II) facilitated the sorption of one another on tire powder through the formation of TC–Cu(II) complexes. Ling et al. inferred that resin–Cu(II) bridging to TC was the leading mechanism for the adsorption of TC.

Adsorption isotherms of Cu(II) on Fe–N,N-SBA15 in the absence and the presence of TC are shown in Fig. 4b. The adsorption amount of Cu(II) on Fe–N,N-SBA15 increased with the increasing equilibrium concentration of Cu(II). Due to the mesoporous structure and amino-groups of the adsorbent, Fe–N,N-SBA15 has great affinity for the chelate ability of Cu(II). The presence of TC increased the adsorption capacity of Cu(II) onto the adsorbent. This result was not consistent with that reported by Kang et al. but agreed with Wang et al. (Kang et al., 2010; Wang et al., 2008). In the Kang et al. results, the adsorption mechanism was due to the formation of Cu(II)/TC–organic complexes on the surface of chitosan. TC competed with Cu(II) for the functional groups on chitosan, leading to less adsorption amount of Cu(II). In our study, the main functional groups of adsorbent were Fe(III) and amino groups, due to the complexation-bridging between Cu(II)–TC and TC–Fe(III) on the adsorbent, the adsorption capacity of Cu(II) was enhanced. Furthermore, as mentioned above, the TC–Cu(II) complex may have stronger affinity on Fe–N,N-SBA15 than TC and Cu(II) separately.

The adsorption data were fitted by Langmuir and Freundlich model isotherm equations, respectively (Ling et al., 2013). The calculated parameters are listed in Table 1. The Langmuir isotherm assumes the adsorbate forms a monolayer around the homogenous surface of the adsorbent and Freundlich model assumes that adsorption takes place on a heterogeneous surface. Compared with the Langmuir model, the Freundlich model fits the adsorption isotherms better ($R^2 = 0.92–0.97$), which indicates that the uptake of TC and Cu(II) on the sorbent is multilayer adsorption. The results were attributed to adsorption site heterogeneity, with possibilities of TC–Fe(III) interaction, TC–Cu(II) interaction and Cu(II)–amino interaction. The values of K_f and $1/n$ for all the results suggested the adsorbent was favorable for the removal of TC and Cu(II) from aqueous solution (Wang et al., 2008).

Fig. 4. Adsorption isotherms of TC and Cu(II) onto Fe–N,N-SBA15. (a) Adsorption isotherms of TC in the absence or presence of Cu(II). Experimental conditions: $[Cu(II)]_0 = 0, 0.25$ or 0.5 mM, $pH = 5.5 \pm 0.1$, $m = 1$ g L^{-1} , $T = 25$ °C. (b) Adsorption isotherms of Cu(II) in the absence or presence of TC. Experimental conditions: $[TC]_0 = 0$ or 0.1 mM, $pH = 5.5 \pm 0.1$, $m = 1$ g L^{-1} , $T = 25$ °C.

Table 1

Langmuir and Freundlich parameters for the adsorption of TC and Cu(II).

Initial concentration (mM)		Langmuir			Freundlich		
		Q_{max} (mmol kg ⁻¹)	b (L mmol ⁻¹)	R^2	K_f (mmol ¹⁻ⁿ L ⁿ kg ⁻¹)	$1/n$	R^2
TC = 0.1	Cu(II) = 0	53.9	104.4	0.90	93.6	0.27	0.92
	Cu(II) = 0.25	92.9	155.7	0.88	192.2	0.38	0.96
	Cu(II) = 0.5	112.3	325.8	0.96	183.8	0.18	0.96
Cu(II) = 0.25	TC = 0	475.1	16.7	0.92	459.4	0.22	0.96
	TC = 0.1	567.0	10.0	0.88	518.4	0.32	0.97

The maximum adsorption capacity (Q_{max}) calculated by the Langmuir models indicated that the presence of Cu(II) and TC facilitated the adsorption of each other on the Fe-N,N-SBA15. These results all indicate that Fe-N,N-SBA15 can remove TC and Cu(II) simultaneously from aqueous solution.

3.5. Adsorption mechanism

FT-IR and XPS analyses are used to investigate the adsorption mechanism of TC and Cu(II) on Fe-N,N-SBA15. FT-IR spectra of virgin and adsorbate-loaded adsorbents are shown in Fig. 5.

TC is an amphoteric molecule and possesses tricarbonylamide, phenolic diketone, and dimethylamine groups (Fig. 5), and the main characteristic peaks of TC are located in the range of 1200–1700 cm⁻¹. As shown in Fig. 5d, the peaks at 1523 cm⁻¹ and 1674 cm⁻¹ are attributed to the vibration of NH₂ amide and C=O amide groups of ring A, respectively. The peaks at 1616 cm⁻¹ and 1456 cm⁻¹ can be assigned to the C=O stretching of ring A and the C–C stretching vibration, respectively (Parolo et al., 2010, 2008). The appearance of these peaks in the spectrum of TC-loaded adsorbent indicated that TC was adsorbed onto the surface of adsorbent. Compared with the TC spectrum, the peaks of the NH₂ amide and C=O amide shifted to lower frequencies, implying interaction between the amide group of TC and Fe(III) on the adsorbent (Fig. 5c). After Cu(II) adsorption, the bands of N–H on the adsorbent shifted slightly, indicating the amino-group plays an important role in the adsorption of Cu(II)

due to the strong chelating capability between Cu(II) and amino groups on the adsorbent (Fig. 5b).

To further investigate the interactions between the adsorbent and adsorbate, XPS characterization of adsorbents before and after the adsorption of TC and Cu(II) were conducted. The wide scan results (Fig. S4) clearly show that the adsorbent is composed of C, N, O and Si elements. After the Cu(II) or TC/Cu(II) adsorption, the appearance of a small peak around 933 eV indicates the adsorption of Cu(II) on the Fe-N,N-SBA15.

The high resolution Fe 2p XPS spectra of Fe-N,N-SBA15 before and after adsorption are shown in Fig. 6. The peak positions of Fe 2p_{3/2} and Fe 2p_{1/2} have been reported to be around 711 and 724 eV, respectively (Grosvenor et al., 2004; Yamashita and Hayes, 2008). After TC loading, the peak of Fe 2p_{3/2} increased from 710.5 eV to 710.9 eV, indicating the interaction between Fe(III) and TC. After Cu(II) uptake, the peak of 710.5 eV (in virgin adsorbent) shifted to 711.4 eV (Cu(II) and TC/Cu(II)-loaded adsorbent). The shift of the binding energy could be attributed to the interaction of Cu(II) and amino groups. When Cu(II) was added into the solution, some of the amino groups on Fe-N,N-SBA15 could combine with Cu(II), as the amino exhibits strong affinity towards Cu(II), therefore inducing an increased binding energy for Fe(III). For the TC/Cu(II)-loaded sample, the binding energy of Fe 2p_{3/2} increased slightly, suggesting that TC–Cu(II) complex formed and influenced the adsorption of TC and Cu(II).

The high resolution N 1s XPS spectra of the adsorbents before and after adsorption are shown in Fig. 6. The peaks at

Fig. 5. FT-IR spectra of (a) Fe-N,N-SBA15; (b) Cu(II)-loaded Fe-N,N-SBA15; (c) TC-loaded Fe-N,N-SBA15; (d) TC.

Fig. 6. The XPS spectra of Fe 2p, N 1s, Cu 2p on (a) Fe-N,N-SBA15; (b) TC-loaded Fe-N,N-SBA15; (c) Cu(II)-loaded Fe-N,N-SBA15; (d) TC/Cu(II)-loaded Fe-N,N-SBA15.

399.3–399.6 eV can be assigned to $-\text{NH}_2$ or $-\text{NH}$, and the peak at 401.4–401.7 eV is assigned to amino perturbed by a positive cation, $\text{NH}_2\text{--Fe(III)}$, which was also observed by Chen et al. (2009), Zuo et al. (2012). After TC uptake, only slight shifts of the two peaks were observed which attributed to the interaction between Fe(III) and amide of TC. When Cu(II) or TC/Cu(II) were added, peaks of $\text{NH}_2\text{--Fe(III)}$ nearly disappeared, and new peaks at 400.2 eV appeared, which proved the adsorption interaction between Cu(II) and amine group (Ling et al., 2013). Due to the strong complexation between Cu(II) and amino groups of the adsorbent, the N atom donated a lone pair electrons to form the covalent bond N--Cu(II) , causing the reduction of electron cloud density and locating at a higher binding energy (Kang et al., 2010; Ling et al., 2013). However, the binding energy of peak of N--Cu(II) on the TC/Cu(II)-loaded sample had a higher energy than that with only Cu(II) loaded, suggesting that the TC–Cu(II) complex participated in a bridging interaction between TC and the adsorbent.

The high resolution XPS spectra of the Cu(II) 2p are shown in Fig. 6. The peaks centered at 933 and 953 eV should be assigned to the binding energy of the Cu(II) $2p_{2/3}$ and Cu(II) $2p_{1/2}$ level, respectively (Wu et al., 2013; Zhao et al., 2013). After Cu(II) uptake, the peak at the binding energy of 932.72 and 934.21 eV was assigned to the signals of Cu(0) and Cu(II), respectively. The presence of Cu(0) was probably caused by the reducing effect of the amino group, which could convert Cu(II) species into Cu (0) (Wu et al., 2013). After TC/Cu(II) uptake, the two peaks of Cu(II) $2p_{2/3}$

shifted to 933.12 and 934.72 eV, respectively, directly proving the formation of TC–Cu(II) complex.

3.6. Recyclability

The reusability of an adsorbent is important for lowering the cost of the adsorption process. For regeneration, 0.1 mM HCl aqueous solution was used as the desorption of TC and Cu(II) from adsorbent. Almost complete desorption of TC and Cu(II) was achieved and the amount of the residual TC and Cu(II) were less than 0.4 mmol kg^{-1} (Table S2). After the acid treatment, most of the organic functional groups were retained and the degree of the residual N was 92.5%, while almost all of Fe(III) leached. We re-introduced Fe(III) to restore the useful adsorption sites, and the degree of restoration of Fe(III) was 96%. The recyclability of the adsorbent was investigated by repeating the adsorption/desorption process 5 times. After the 5th adsorption/desorption cycle, the adsorption capacity of TC and Cu(II) onto the adsorbent was approximately 88.5% and 94.1% of the initial adsorption amounts, respectively (Fig. S5). The adsorbent exhibited good reusability due to the large pore size, high ratio of meso-pore volume and abundant useful adsorption sites.

4. Conclusions

A novel mesoporous silica adsorbent contained amino groups and coordinated Fe(III) was prepared by grafting method. The

adsorbent preserve the mesoporous structural order after the functionalization of the amino/metal groups. The resultant adsorbent could be used in adsorption and cosorption of TC and Cu(II) from aquatic environment. Owing to dual-functional groups, Fe-N,N-SBA15 had high affinity adsorption for both TC and Cu(II), and synergistic effects on adsorption were found. Increasing adsorption of TC and Cu(II) on the adsorbent could be attributed to the formation of complex TC–Cu(II) bridging or the stronger affinity of the adsorbent for the TC–Cu(II) complex than that TC or Cu(II) separately. Results also showed that Fe(III) and amino groups on the adsorbent were complexed with the amide of TC and Cu(II), respectively. The results also suggest that Fe-N,N-SBA15 is a reusable efficient adsorbent for TC and Cu(II) removal. This work provides an effective method for the simultaneous removal of antibiotics and heavy metals from aquatic environments.

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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.chemosphere.2015.07.014>.

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