

Chemical adsorption of oxytetracycline from aqueous solution by modified molecular sieves

Junmin Lv, Yulong Ma, Xuan Chang, Junzhuo Fang, Lingyan Cai, Yan Ma and Subing Fan

ABSTRACT

The removal of oxytetracycline (OTC) from aqueous solution on modified molecular sieve via adsorption was investigated in the present work. The copper(II) modified molecular sieve had the much higher adsorbed amount than unmodified one. The bigger pore, the more adsorption sites benefitted for the adsorbed amount of OTC. The exchanged amount of copper(II) and the acid-base property of solution were important factors influencing the removal efficiency. The adsorption kinetics, the adsorption isotherm, the adsorption thermodynamics and the proposed adsorption mechanism were studied. The analysis of adsorption isotherm indicated it is a monolayer adsorption. The fitting with adsorption kinetics, pseudo-second-order model, deduced chemical adsorption is the main rate controlling step. And the new formation of Cu-O chemical bond and the changes at bands of N-H vibration and C-N vibration by Fourier transform infrared spectrometer further confirmed the proposal adsorption mechanism was the chemical complexation of copper(II) in modified 13X with NH₂ group of OTC. As the real exchanged amount of copper(II) was 149.07 mg·g⁻¹ and the solution pH 7.0, the adsorption capacity of modified 13X for OTC reached the maximum of 2,396 mg·g⁻¹ (with the initial concentration of 1,000 mg·L⁻¹).

Key words | adsorption behaviors, adsorption mechanism, chemical adsorption, modified molecular sieve, oxytetracycline

Junmin Lv
Xuan Chang
Junzhuo Fang
Lingyan Cai
Yan Ma

Subing Fan
State Key Laboratory Cultivation Base of Energy Sources and Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China

Yulong Ma (corresponding author)
State Key Laboratory Cultivation Base of Energy Sources and Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Helanshan Rd. 539, Yinchuan 750021, China
E-mail: yulongma796@sohu.com

INTRODUCTION

Antibiotics have a positive effect for the health of humans and animals, but their residues, which subsequently transfer into the aquatic environment and soil from bodies in various ways and eventually pollute the underground water and even our drinking water (Alighardashi *et al.* 2008; Belaib *et al.* 2014), will cause the resistant microorganisms and bring a great threat to human health by increasing the risk of certain infections (Chen & Yang 2006; Paul *et al.* 2007; Locatelli *et al.* 2011). Oxytetracycline (OTC) is one of tetracycline (TC)-antibiotics and is used worldwide for diseases treatment, diseases prevention and growth promotion in livestock (Zhao *et al.* 2014). OTC residues mainly include the wastewater discharge from pharmaceutical manufacture and other residues in agriculture and livestock farming (Watkinson *et al.* 2009; Milić *et al.* 2013). The presence of OTC in surface water has been proved at levels up to a few micrograms per litre and even milligrams per litre (Li

et al. 2008). Because of the stability of the naphthalene ring structure, solubility in water and toxicity to the microorganism, OTC is difficult to degrade by biodegradation or conventional treatment processes (Zhao *et al.* 2010; Pereira *et al.* 2011). Therefore, it is necessary to develop an effective method to remove the OTC residues that exist in the environment, especially in aqueous solution which is directly relative with drinking water.

Various physico-chemical treatment methods have been used to remove OTC in the water environment (Belaib *et al.* 2014). Oxidative degradation has high removal efficiency, but would bring secondary pollution and secondary pollution often has a more serious impact on the environment (Zhao *et al.* 2010). Photo-catalysis process also proved very efficient to remove some antibiotics, while the light source with high energy and the high effective catalyst are required and large-scale application is still limited (Homem & Santos 2011;

Daghrir & Drogui 2013). In contrast, the adsorption process shows more advantages of being secondary pollution-free, reproducibility and higher adsorption efficiency, which make it be an effective, environmentally-friendly and low-cost process (Wang *et al.* 2010; Jia *et al.* 2013; Belaib *et al.* 2014).

The electron donating radical of OTC molecule is easy to coordinate with some metal ions (MacKay & Canterbury 2005; Jin *et al.* 2007). Liu *et al.* (2014) investigated the adsorption behaviors of OTC onto soils when copper(II) exists, and the results showed that the presence of copper(II) could increase the uptake of OTC from pH 3.0 to 10.0. TC and OTC all belong to TC-antibiotics and contain amino and hydroxyl groups in the structure. Wang *et al.* (2008) studied the effect of copper(II) of solution on the adsorption of TC onto the surface of montmorillonite and the results showed that coexistence of TC and copper(II) enhanced its adsorption on montmorillonite in a certain pH range.

Molecular sieve with ordered pore structure and large specific surface area belonging to porous material have excellent catalytic and adsorption performance, which have a wide range of applications in many fields such as agriculture and industry (Xu 2011; Jiang *et al.* 2012; Liu *et al.* 2013). Moreover, it has excellent cation exchange capacity, which could be modified to get more selective adsorption sites and to enhance its adsorption capacity.

In the present work, several molecular sieves were modified by ion-exchange with copper(II) rather than loaded by CuO form, which could enhance the removal of OTC from aqueous solution by selective adsorption instead of free diffusion. Batch experiments were carried out to research the influences of adsorption conditions, the adsorption isotherms, kinetics and thermodynamics. The adsorption mechanism was also further studied. Up to now, there are few reports about removing OTC from aqueous solution by modified molecular sieves.

MATERIALS AND METHODS

Materials

OTC (98%, stored in dark at 4 °C), Acetonitrile (HPLC grade, 99.9%) and Methanol (HPLC grade, 99.9%) were obtained from Beijing Lark Technology Co., Ltd of China. NaOH (AR, 96%), hydrochloric acid (AR, 36–38%), and Cu(NO₃)₂·3H₂O (AR, 99%) were commercial reagents and used as received. Microporous molecular sieves (Y, 13X, 4A) were purchased from Dalian Absorbent Co., Ltd of China.

Preparation of adsorbent

2 g of molecular sieve (4A, Y and 13X) was respectively added to 100 mL of different concentrations of copper nitrate solutions in a 250 mL flask. The initial concentrations of copper nitrate were 0, 0.25, 0.5, 1.5 and 2.5 g per gram of 13X, respectively. Then, the suspension liquid was refluxed at 80 °C under stirring for 3 h, followed by filtered and washed with hot deionized water until no copper(II) was detected in filtrate. The ion-exchange process was repeated three times. Finally, the obtained solids were dried at 80 °C overnight in air (Salama *et al.* 2006; Fathima *et al.* 2008) and were marked as modified 4A(x), modified Y (x) and modified 13X(x), where x was the mass of the copper salt per gram of molecular sieve.

Characterization and analysis

The X-ray diffractions (XRD) of synthesized materials were characterized on a Rigaku D/Max 2200 diffractometer with Ni-filtered CuK α radiation at 40 kV and 30 mA. Samples were scanned from 3 ° to 50 ° of 2 θ (at 8 ° min⁻¹ with a scanning step of 0.02 °). Atomic absorption spectroscopy was used to analyze the real exchanged amount of copper(II). The real exchanged amount of copper(II) was calculated with the difference between total copper(II) amount and the amount of copper(II) in the eluent. The adsorbents were marked as modified 4A [y], modified Y [y] and modified 13X [y]; here y was the real exchanged amount of copper(II). The adsorption mechanism was studied via infrared spectrum recorded on a Fourier Transform Infrared spectrometer of Bruker Tensor 27 with the resolution of 2 cm⁻¹.

Adsorption experiments

Batch adsorption experiments of OTC from aqueous solution by using modified molecular sieves were carried out. 100 mL solution with a designed concentration of OTC was added to the flask and then was adjusted to a designed pH value with NaOH solution (0.10 mol·L⁻¹ for 50–200 mg·L⁻¹ of OTC solution, and 1.0 mol·L⁻¹ for 400–1,000 mg·L⁻¹ of OTC solution) at a designed temperature. 0.04 g of modified molecular sieve as adsorbent was then added to the above solution. Next, the flask was sealed with aluminum foil and stirred (120 rpm) continuously in the dark place. About 0.5 mL of filtrate was collected with 0.22 μ m membrane at a selected time intervals to analyze the removal efficiency using high-performance liquid chromatography (HPLC) until the adsorption reached equilibrium.

Analysis method

The analysis of the removal efficiency

The removal efficiency was analyzed using HPLC of the 364 nm determination wavelength. The adsorption capacity and the removal efficiency are calculated using Equations (1) and (2) (Choi et al. 2008) as follows:

$$q_e = (C_0 - C_e) \times \frac{V}{W} \quad (1)$$

$$\alpha = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where q_e ($\text{mg}\cdot\text{g}^{-1}$) is the adsorption capacity in modified molecular at the equilibrium; α is the removal efficiency; C_0 and C_e ($\text{mg}\cdot\text{L}^{-1}$) are the initial and equilibrium concentrations of solution, respectively; V (L) is the volume of the aqueous solution and W (g) is the mass of adsorbent used in the experiments.

Adsorption kinetics

The experiments of adsorption OTC were conducted at different initial concentrations of 50, 100, 200, 400, 700 and 1,000 $\text{mg}\cdot\text{L}^{-1}$, respectively. The dosage of modified 13X [149.07 $\text{mg}\cdot\text{g}^{-1}$] was 0.04 g. The temperature was 308 K and the initial pH was 7.0. Blank experiment was also carried out with the unmodified 13X molecular sieve. Three adsorption kinetic models, i.e. the pseudo-first-order model, the pseudo-second-order model and the intra-particle diffusion model, were applied to interpret the experimental results.

The pseudo-first-order model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

The pseudo-second-order model:

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

The intra-particle diffusion model:

$$q_t = k_3 t^{1/2} + C \quad (5)$$

where k_1 (min^{-1}) is the first-order rate constant; k_2 ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) is the second-order rate constant; k_3 ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$) is the intra-particle diffusion rate constant;

C ($\text{mg}\cdot\text{g}^{-1}$) is a constant that is about the thickness of the boundary layer; q_e and q_t ($\text{mg}\cdot\text{g}^{-1}$) are the amount of OTC adsorbed at the equilibrium and at time t (min), respectively.

Adsorption isotherms

The adsorption experiments were carried out at different temperatures (298, 308, and 318 K). The concentrations of OTC in aqueous solutions were 100, 200, 300, 400, 500, 700 and 1,000 $\text{mg}\cdot\text{L}^{-1}$. The Langmuir and Freundlich equations are commonly used in the adsorption of antibiotics on several adsorbent systems (Brigante & Schulz 2011). The equations of the models are described as follows.

Langmuir isotherm:

$$q_e = \frac{q_{\max} K_L C_e}{(1 + K_L C_e)} \quad (6)$$

Freundlich isotherm:

$$q_e = k_f (C_e)^{1/n} \quad (7)$$

The linear forms of these isotherms equations:

$$\frac{1}{q_e} = \frac{1}{(q_{\max} K_L)} \times \left(\frac{1}{C_e} \right) + \frac{1}{q_{\max}} \quad (8)$$

$$\lg(q_e) = \lg(k_f) + \frac{1}{n} \times \lg(C_e) \quad (9)$$

where q_e ($\text{mg}\cdot\text{g}^{-1}$) is the amount of TC adsorbed on the adsorbent at the equilibrium. q_{\max} ($\text{mg}\cdot\text{g}^{-1}$) is the maximum adsorption, which is used to describe the adsorption capacity. K_L is the Langmuir adsorption equilibrium constant and C_e ($\text{mg}\cdot\text{L}^{-1}$) is the concentration of equilibrium solution. k_f ($\text{mg}\cdot\text{g}^{-1}\cdot(\text{L}\cdot\text{mg}^{-1})^{1/n}$) is Freundlich constant. $1/n$ is the adsorption intensity.

Adsorption thermodynamics

The thermodynamic equilibrium constant K for the sorption reactions was determined by plotting $\ln(q_e/C_e)$ vs. q_e and extrapolating to zero q_e to get the $\ln(q_e/C_e)$ (Khan & Singh 1987; Raji & Anirudhan 1998). K was calculated according to the formula (10).

The standard free energy change ΔG was determined using the equations (11). By plotting $\ln K$ vs. $1/T$ of the equations (12), the slope and intercept of straight line are

used to calculate the values of enthalpy change ΔH and entropy change ΔS .

$$\lim_{n \rightarrow \infty} (q_e/c_e) = K \quad (10)$$

$$\Delta G = -RT \ln K \quad (11)$$

$$\ln K = \frac{\Delta H}{(-RT)} + \frac{\Delta S}{R} \quad (12)$$

RESULTS AND DISCUSSION

Comparison of three modified molecular sieves

XRD characterization of three modified molecular sieves

X-ray diffraction spectra of three modified molecular sieves with copper(II) are shown in Figure 1. The dosage of the

copper nitrate was set as 0, 0.25, 0.50, 1.50 and 2.50 $\text{g}\cdot\text{g}^{-1}$ (molecular sieve). When the dosage of copper nitrate was less than 0.50 $\text{g}\cdot\text{g}^{-1}$ (molecular sieve), the characteristic peaks of three molecular sieves remained, demonstrating that the skeleton structure of three molecular sieves was preferably retained. When the dosages of copper nitrate were between 0.50 and 2.50 $\text{g}\cdot\text{g}^{-1}$ (molecular sieve), the structure of Y and 13X still remained, although the intensities of their characteristic peaks decreased. However, for 4A molecular sieve, when the dosage of copper nitrate was more than 1.50 $\text{g}\cdot\text{g}^{-1}$ (molecular sieve), the characteristic peaks of copper species apparently appeared, meanwhile that of framework structure decreased greatly. So, three modified molecular sieves with copper nitrate of 0.50 $\text{g}\cdot\text{g}^{-1}$ (molecular sieve) were chosen to adsorb OTC from aqueous solution and to compare their adsorption performance.

Adsorption performance on three modified molecular sieves

Figure 2 shows the adsorption performance to OTC on three different modified molecular sieves. The adsorbed amount

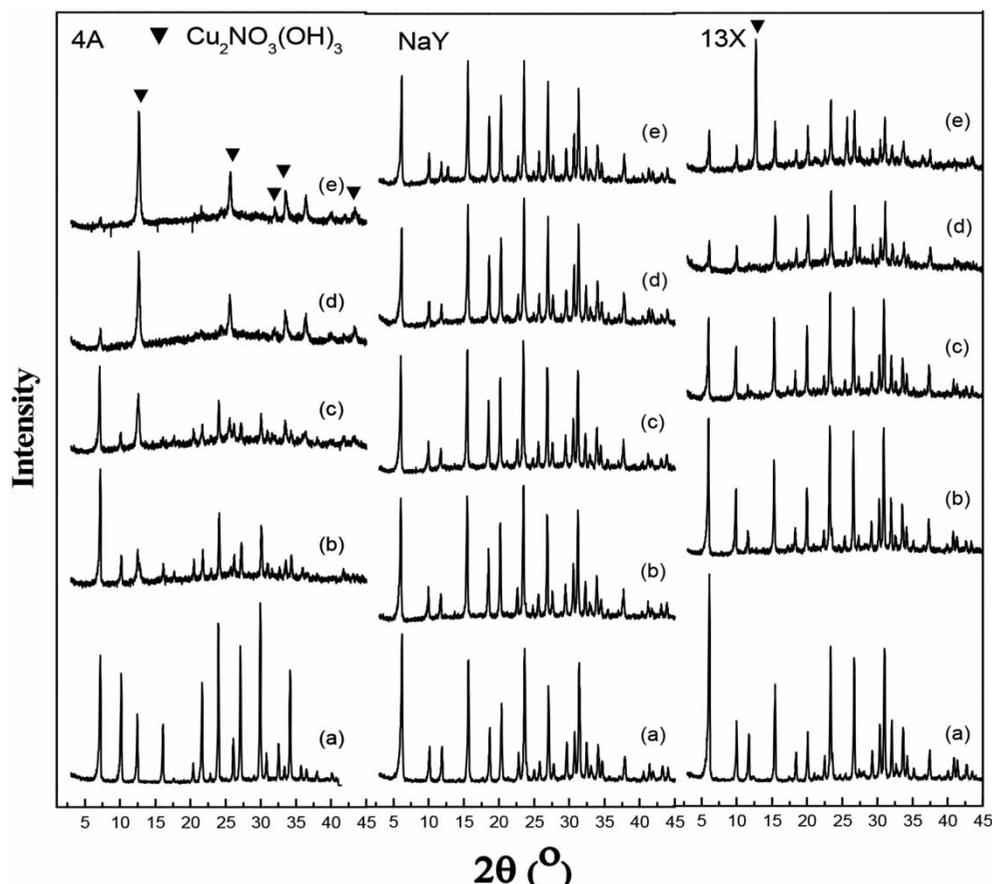


Figure 1 | XRD patterns of modified molecular sieves with different dosage of copper(II). The dosages of copper(II) were (a) 0, (b) 0.25, (c) 0.5, (d) 1.5, and (e) 2.5 $\text{g}\cdot\text{g}^{-1}$ (molecular sieve).

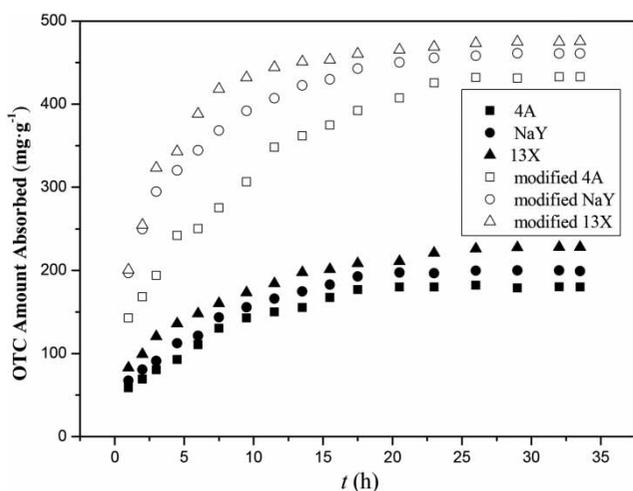


Figure 2 | Adsorption efficiency of three modified molecular sieves. The dosage of copper nitrate: $0.5 \text{ g} \cdot \text{g}^{-1}$ (molecular sieve); initial concentration of OTC: $200 \text{ mg} \cdot \text{L}^{-1}$; 308 K, pH 7.0.

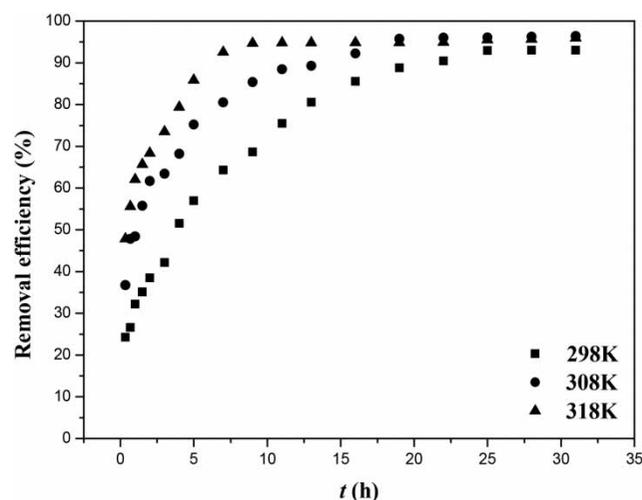


Figure 3 | The influences of contact time and temperature on adsorption of OTC on modified 13X.

of OTC on every modified molecular sieve was much higher than that on corresponding unmodified one. The modified 13X had the highest removal efficiency of about 95% and the biggest adsorption capacity of $475 \text{ mg} \cdot \text{g}^{-1}$, while the modified Y and the modified 4A had the lower removal efficiency and smaller adsorption capacity. The adsorbed amount of every adsorbent sample followed the order that: $4\text{A} < \text{NaY} < 13\text{X}$, whether it was modified or not, which might be related to adsorption sites and pore diameter. 13X with bigger pore diameter (about 1.0 nm) had the greater adsorption capacity than 4A (only 0.4 nm) although they had a similar number of adsorption sites relating to silica alumina ratio (about 2.0), indicating the bigger pore diameter benefited the diffusion of OTC into pores of molecular sieve and the effect was remarkable. In addition, as 13X and Y had bigger pore diameters, the higher adsorption amount on 13X was attributed to its greater number of adsorption sites (silica alumina ratio was 2.0 and 6.0, respectively). Thus, the following experiments were carried out with the modified 13X as adsorbent.

Influence of adsorption conditions

Influence of contact time and temperature

The influence of contact time and temperature on the adsorption of OTC is shown in Figure 3. The adsorption experiments were conducted at the temperatures of 298 K, 308 K and 318 K. The concentration of OTC aqueous solution was $200 \text{ mg} \cdot \text{L}^{-1}$. The solution was continuously

stirred at the initial pH 7.0 when the adsorbent was added. Time was one of the important factors that affected the adsorption equilibrium. The OTC removal efficiency of modified molecular sieve increased quickly at the beginning of adsorption, and then gradually flattened out until the adsorption equilibrium, because when the adsorbent of modified molecular sieve was added to the solution, the difference in OTC concentration between the modified molecular sieve surface and the solution was the largest, resulting in the largest adsorption driver. With the passage of time, the concentration difference gradually decreased, thus abating the adsorption driver and the adsorption process tends to reach equilibrium (Chen 2008).

As seen in Figure 3, the adsorption rate of OTC at 318 K was obviously the fastest, suggesting that high temperature provided high energy for OTC molecules to reach the balance of adsorption and desorption on the surface of adsorbent. With the increase of contact time, the removal efficiency quickly increased and tended to balance after about 9 h at 318 K, while the balance time at 308 K and 298 K was 19 h and more than 25 h, respectively. The final removal efficiency at three temperatures was very close, which might contribute to the exothermic chemical adsorption discussed later.

Influence of the copper(II) exchange amount

In order to study the role of copper(II) on the removal efficiency of OTC over 13X, parallel experiments were carried out at the temperatures of 308 K and pH 7.0. The initial concentrations of OTC were $400 \text{ mg} \cdot \text{L}^{-1}$. The OTC removal

efficiency with different exchange amount of copper(II) on 13X is shown in Table 1. Compared with 13X without exchanging copper(II), the removal efficiency of 13X with exchanging copper(II) was far greater, indicating that the exchanged copper(II) had an important influence on adsorption of OTC. With the increase of exchanged copper(II), the OTC removal efficiency of modified 13X increased. When the actual exchange amount of copper(II) reached $149 \text{ mg} \cdot \text{g}^{-1}_{13\text{X}}$, the removal efficiency was above 99%. And when the dosage of copper(II) continually increased, the real content of copper(II) of modified 13X and the OTC removal efficiency were almost unchanged. So, modified 13X with the exchange amount of copper nitrate of $1.00 \text{ g} \cdot \text{g}^{-1}_{13\text{X}}$ was chosen for the following investigation of adsorption conditions.

Influence of acid-base property of solution

OTC contains amphoteric functional groups. Different acid-base property of solution results in the different form and charge of OTC. The solutions were prepared with $100 \text{ mg} \cdot \text{L}^{-1}$ of OTC and different initial pH values were set at 3.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 11.0, respectively. The influence of acid-base property of solution on the OTC removal efficiency is shown in Figure 4. The OTC removal efficiency increased with the adsorption time. The OTC removal efficiency after adsorbing for 14 h follows the order of pH value: $7.0 > 6.0 > 5.0 > 8.0 > 9.0 > 11.0 > 3.0$.

The pK_a values of OTC are 3.57, 7.49 and 9.88, respectively (Zhao *et al.* 2010). When the pH was below 3.57, the dimethyl-ammonium group is protonated, resulting in a cationic form (OTCH_3^+). Electrostatic repulsion of OTCH_3^+ and

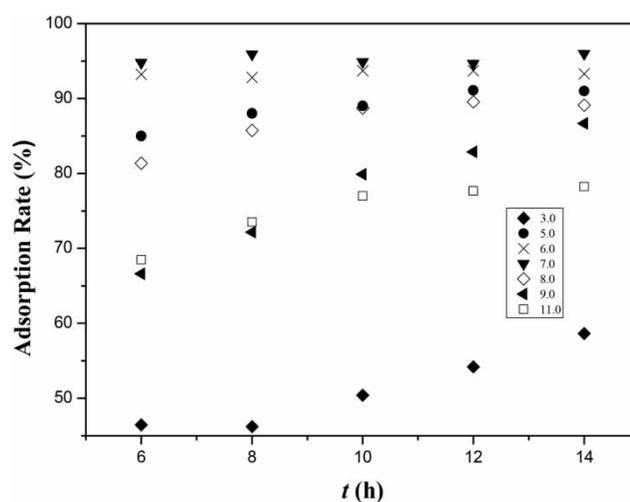


Figure 4 | The influence of initial pH value on the removal efficiency of OTC.

Cu^{2+} result in the decreasing of the removal efficiency of OTC. In addition, the copper(II) cation in the framework of modified 13X would also be exchanged out under the strong acid condition and greatly decreased its adsorption efficiency. When the pH value increased from 3.57 to 5.50, the cationic (OTCH_3^+) gradually disappeared while its zwitterionic form of OTCH_2^0 gradually increased to be dominant due to the loss of proton from the phenolic diketone moiety. The adsorption of OTC gradually increased because of the decrease in the electrostatic repulsion between copper(II) and the cationic OTCH_3^+ . At the pH above 5.50, its anionic form produced and took up the dominant position gradually, especially at pH above 7.49, and the form of OTCH_2^0 decreased gradually until zero (at pH of about 9.40) (Zhao *et al.* 2010; Wang *et al.* 2014; Zhang *et al.* 2014). Then, theoretically, the negative charge of OTC benefits the selective adsorption of modified 13X. However, when the solution pH was above 7.0, desilication in the framework of modified molecular sieve would partially happen and lead some copper(II) ions in the modified 13X transferring into the solution, then resulting in decreasing the adsorption of OTC. Hence, the pH of solution is one of the very important factors affecting the adsorption process.

Adsorption kinetics

The adsorption kinetics experiments under various concentrations of OTC were carried out. Surprisingly, the equilibrium adsorption amount of OTC reached $2,396 \text{ mg} \cdot \text{g}^{-1}$ under the concentrations of OTC $1,000 \text{ mg} \cdot \text{L}^{-1}$. The experimental results were fitted with several kinetic models. While the plot of $\ln(q_e - q_t)$ vs. time t did not show linear relationship,

Table 1 | The relationship between copper(II) content and removal efficiency of modified 13X^a

	Dosage of copper nitrate ($\text{g} \cdot \text{g}^{-1}_{13\text{X}}$)	Real content of copper(II) ($\text{mg} \cdot \text{g}^{-1}_{13\text{X}}$)	Removal efficiency %
M1	0	0	48.03
M2	0.25	66.12	85.98
M3	0.45	115.52	90.36
M4	0.58	146.94	97.95
M5	0.75	148.33	98.77
M6	1.00	149.07	99.21
M7	1.50	149.25	99.13
M8	2.00	149.38	99.18
M9	2.5	-	-

^aM1-M9 represent various samples of modified 13X.

which verified that the adsorption kinetic on modified 13X did not follow the pseudo-first-order equation.

According to the pseudo-second-order model and the intra-particle diffusion model, the experimental data of seven initial OTC concentrations were fitted by making

the plot of t/q_t vs. t and q_t vs. $t^{1/2}$, respectively. From the results given in Figure 5 and Table 2, the R^2 of the linear form for pseudo-second-order model were greater than 0.999, which indicated the pseudo-second-order model is more suitable to describe the adsorption behaviors of OTC

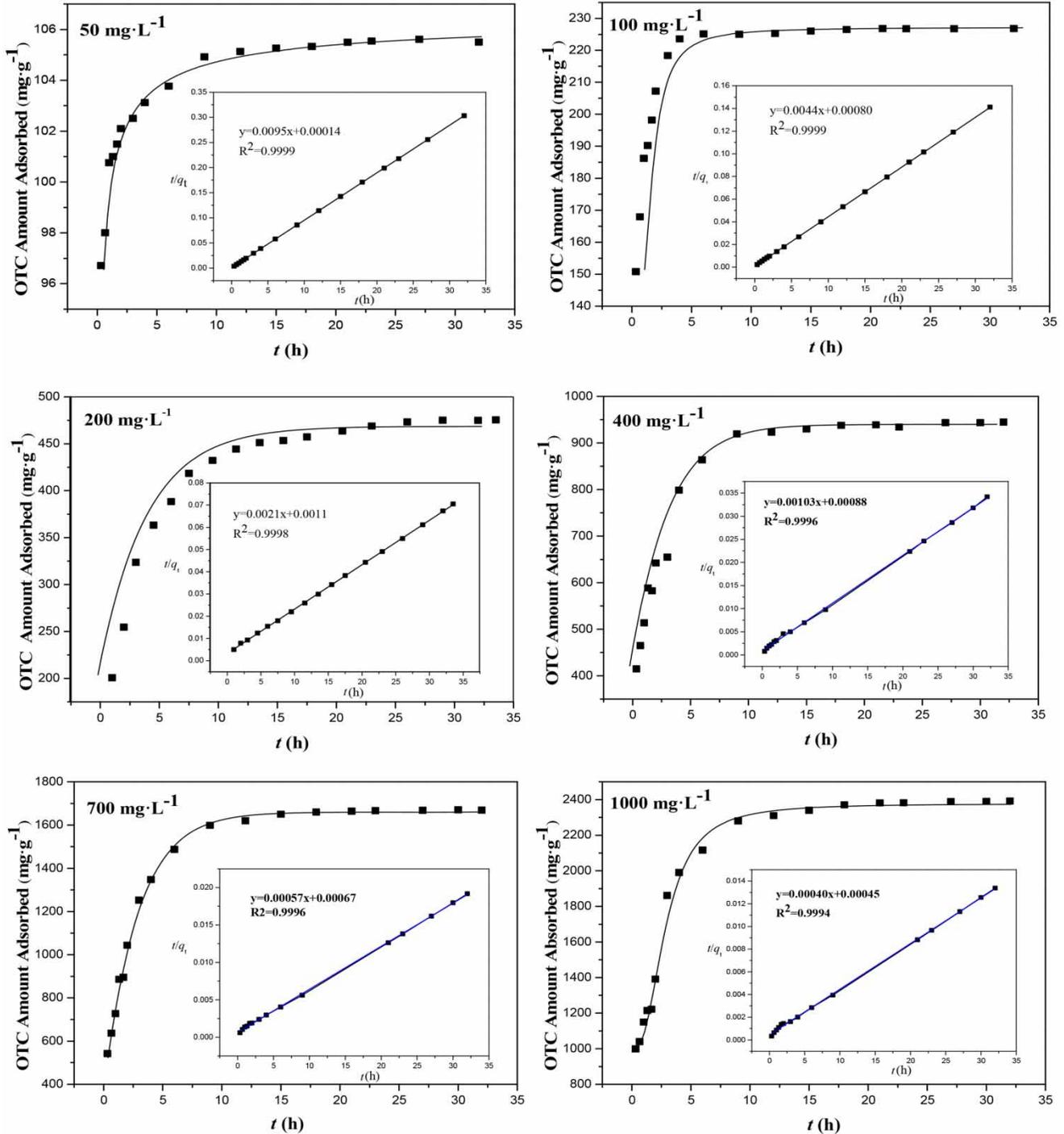


Figure 5 | Adsorption kinetics (50, 100, 200, 400, 700, 1,000 mg·L⁻¹) of OTC and linear fitted by pseudo-second-order kinetics model.

Table 2 | The fitted parameters by pseudo-second-order model and intra-particle diffusion model

Kinetic model	Parameters	C_0 (mg·L ⁻¹)					
		50	100	200	400	700	1,000
Pseudo-second-order model	$q_e/\text{mg}\cdot\text{g}^{-1}$	105.71	232.02	469.48	970.87	1,754.39	2,500.00
	$K_2 \times 10^{-4}/\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	625.79	185.76	40.87	12.06	4.85	3.56
	R^2	0.9999	0.9997	0.9998	0.9996	0.9996	0.9994
Intra-particle diffusion model	$K_3/\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	0.96	40.23	96.33	143.53	215.89	353.91
	$C/\text{mg}\cdot\text{g}^{-1}$	98.70	140.81	201.43	409.90	672.90	937.02
	R^2	0.9150	0.8784	0.9427	0.8323	0.8032	0.8164

on modified 13X and chemical adsorption was the main rate controlling step in the process of OTC adsorption (Ho & McKay 1999; Li *et al.* 2016). The intra-particle diffusion model was used to investigate the diffusion controlling mechanism involved in the OTC adsorption process (Wang *et al.* 2008). When the $q_t t^{1/2}$ curve shows a good linear relationship and passes through the origin of coordinates, then the intra-particle diffusion was the only rate-controlling step in the adsorption process. If the linear is fitted better, but does not pass through the origin, intra-particle diffusion is the rate-controlling step, but not the only one. If the fitting line of q_t vs. $t^{1/2}$ shows multiple linear, it suggests that there are multiple steps in the adsorption process (Chen 2008; Chen 2012). In the experiment, the $q_t t^{1/2}$ curve of initial concentration from 50 to 1,000 mg L⁻¹ OTC were multiple linear figures (as shown in Figure 6), indicating there was more than one control step involved in the process of adsorption OTC. In the beginning stage, the rapid rise was due to the membrane diffusion. Slowly rising stage, the second stage, includes the intra-particle diffusion and surface chemical adsorption. The intra-particle diffusion is the rate-control step. Then, the adsorption sites decrease, the concentration of OTC lowers, the adsorption amount on internal surface increases, and the boundary layer thickens, which resulted in the decreasing of intra-particle diffusion rate and it enters into the final equilibrium stage (Yousef *et al.* 2011).

Adsorption isotherm

The Langmuir model supposes that adsorption occurs only on the homogeneous surface to form monolayer adsorption and there are not interactions between adsorbed molecules. Freundlich model is an experiential adsorption isotherm happening on the heterogeneous surface and can well explain the experimental results in a broader range of concentration.

Adsorption isotherm was adopted to determine the interactions between OTC and modified 13X. The parameters of Langmuir and Freundlich model listed in Table 3 were calculated according to the linear fitting of $1/q_e$ vs. $1/C_e$ and $\log q_e$ vs. $\log C_e$, respectively. The adsorption process of OTC on modified 13X is fitted well with both Langmuir isotherm model and Freundlich isotherm model. But in contrast, the Langmuir isotherm model fit it better. That means the adsorption of OTC on modified 13X is a monolayer adsorption, and the surface of adsorbent is relatively homogeneous which coincide with the uniform structure unit of 13X molecular sieve.

The very high adsorption quantity of 2,304 mg·g⁻¹ on modified 13X indicated it is an effective adsorbent to remove OTC from aqueous solution.

Adsorption thermodynamics

The adsorption thermodynamics equilibrium constant K is calculated according to intercepts of the fitting line of $\ln(q_e/C_e)$ vs. q_e and the formula (10). Thermodynamic parameters are calculated according to formula (11) and (12) and the results are listed in Table 4. The decreased K values and the negative enthalpy change with the increase of adsorption temperature indicated the adsorption was an exothermic process, which resulted in the close removal efficiency at different temperatures as seen in Figure 3. The values of standard Gibbs free energy change (ΔG) were negative, suggesting that the adsorption process was spontaneous. The negative entropy change ΔS demonstrated that the system degree of freedom was decreasing, which meant the system was in order when OTC was adsorbed on the surface of modified 13X.

Proposed adsorption mechanism

Infrared spectrums of ion-exchanged modified 13X samples with and without adsorption of OTC were recorded to under

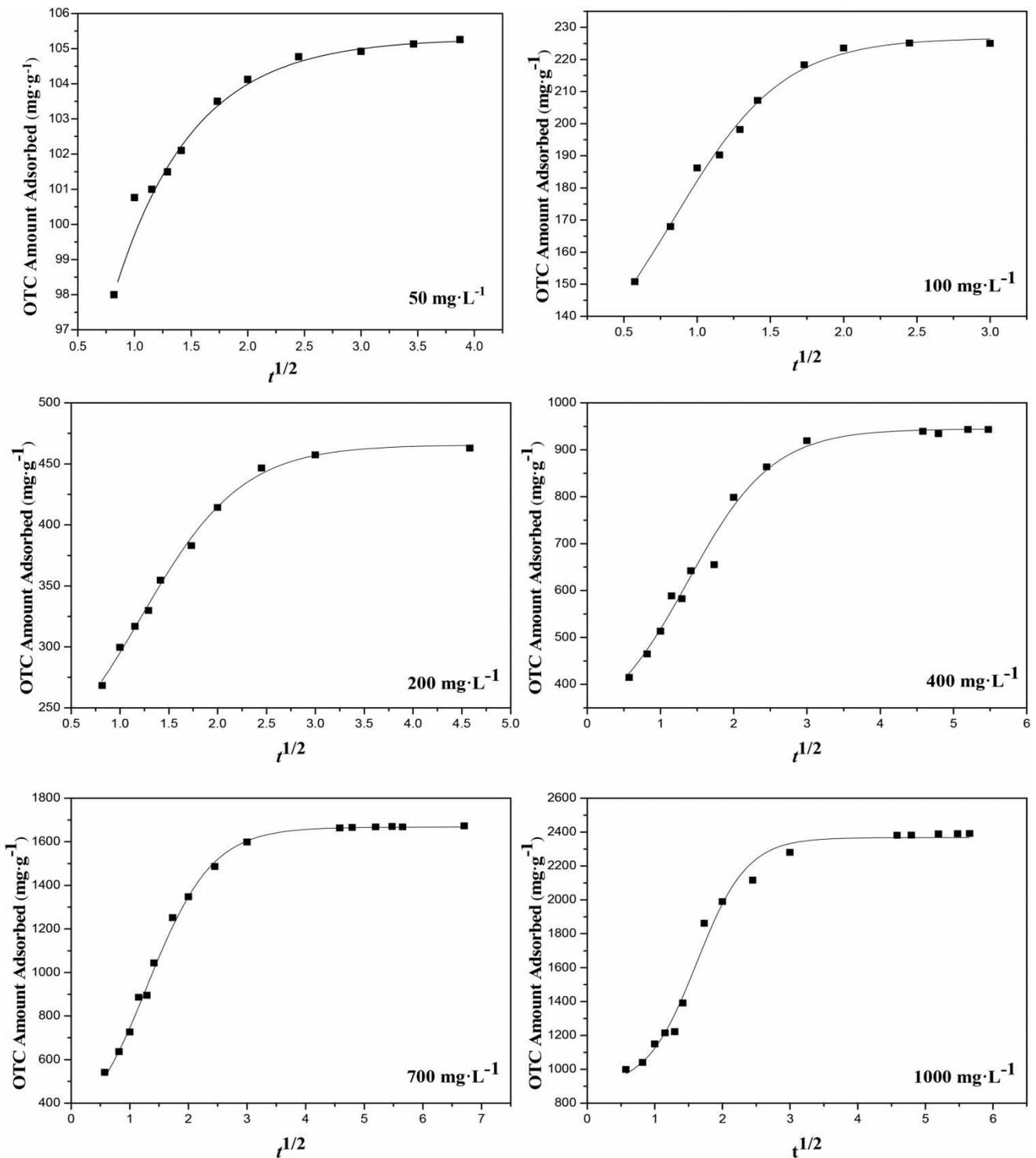


Figure 6 | Linear fitted by intra-particle diffusion model (50, 100, 200, 400, 700, 1,000 mg·L⁻¹).

the adsorption mechanism of OTC on modified 13X (see Figure 7) and the changes of bands were listed in Table 5. When 13X molecular sieve was ion-exchanged with copper(II) cation, a new band of 903.15 cm⁻¹ assigned to

Cu-O bond was found. Meanwhile, the band of 978.82 cm⁻¹ assigned to Si-O shifted to 989.01 cm⁻¹, indicating the stronger interaction happened. That the band of 3,471.51 cm⁻¹ weakened might be due to the reduction of

Table 3 | The fitted parameters of adsorption isotherms

T/K	Langmuir			Freundlich		
	q_{\max} ($\text{mg}\cdot\text{g}^{-1}$)	K_L ($\text{L}\cdot\text{mg}^{-1}$)	R^2	K_f ($\text{mg}\cdot\text{g}^{-1}$ · ($\text{L}\cdot\text{mg}^{-1}$) ^{1/n})	n	R^2
298	2,070	0.1429	0.9944	11.93	1.73	0.9878
308	2,155	0.1552	0.9973	11.52	1.69	0.9895
318	2,304	0.1589	0.9911	11.04	1.26	0.9873

Table 4 | The calculated thermodynamic parameters

T/K	K	ΔG ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔS ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	ΔH ($\text{kJ}\cdot\text{mol}^{-1}$)
298	44.70	-9.41	-47.69	-23.64
308	34.47	-9.07		
318	24.78	-8.49		

hydroxyl group of (Si)-O-H(-Al), suggesting the replacement of H^+ located on (Si)-O-H(-Al) group with copper(II). In addition, the framework vibrations such as the band of 674.35, 566.31, 466.76 cm^{-1} weakening or shifting red was accompanied. After adsorption of OTC, the spectrum of

modified 13X changed somewhere compared with that of OTC and the modified 13X before adsorption. First, compared with modified 13X before adsorption, the framework vibrations shift blue, suggesting the charge of framework reduced due to the interaction between modified 13X and OTC. The changes at bands of N-H vibration and C-N vibration clearly indicated the adsorption was performed through the interaction of NH_2 group of OTC with modified 13X. The band of 903.15 cm^{-1} assigned to Cu-O of modified 13X shifted to 912.19 cm^{-1} , which might evidence that the proposed adsorption mechanism was the chemical complexation of copper(II) in modified 13X with NH_2 group of OTC.

CONCLUSIONS

Adsorption is an effective, environmental-friendly and low cost process. For the OTC in the aqueous solution (instead of wastewater discharge from pharmaceutical manufacture and other residues in agriculture and livestock farming) in this study, the bigger pore and the more adsorption sites made the modified 13X molecular sieve have higher

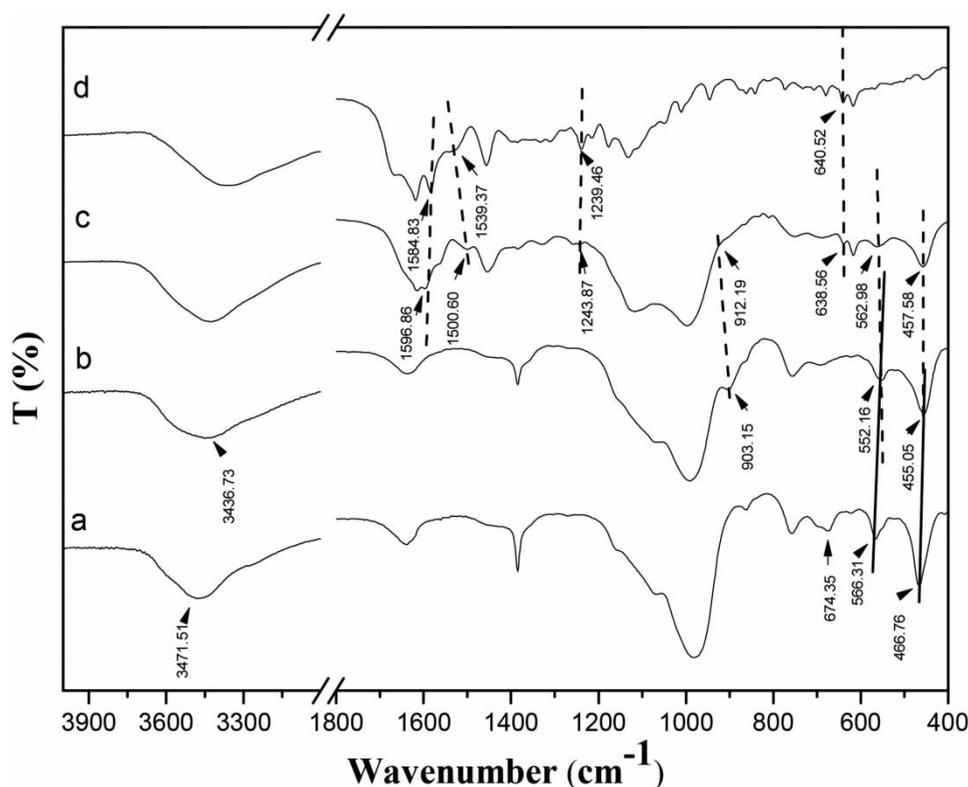
**Figure 7** | The infrared spectra of modified 13X before and after adsorption of OTC. (a) 13X; (b) modified 13X; (c) modified 13X after adsorption of OTC; (d) OTC.

Table 5 | The changes of IR bands comparing after with before adsorption of modified 13X

13X (cm ⁻¹)	modified 13X (cm ⁻¹)	OTC (cm ⁻¹)	modified 13X after adsorption (cm ⁻¹)	assignment
	903.15		912.19	Cu-O
674.35	weaken			framework
566.31	552.16		562.98	framework
466.76	455.05		457.58	framework
978.82	989.01		996.38	Si-O
3,471.51	weaken			(Si)-O-H(-Al)
		1,584.83	1,596.86	N-H deformation
		1,539.37	1,500.62	N-H bend
		1,239.46	1,243.87	C-N stretching
		640.52	638.56	N-H stretching

adsorbed amount of OTC than modified 4A and NaY. The copper(II) modified 13X had been proven to be an effective adsorbent because of the very high adsorption capacity of 2,396 mg·g⁻¹. The amount of copper(II) and the acid-base property of solution were important factors. The chemical adsorption was the main rate controlling step in the process of OTC adsorption and the diffusion control step was multiple steps, as demonstrated by the intra-particle diffusion model. The adsorption process was a monolayer adsorption, and it was exothermic, spontaneous and freedom-decreasing process. The further study showed that this adsorption process might be carried out through the complexation between copper(II) ion of modified 13X and NH₂ group of OTC molecule.

ACKNOWLEDGEMENTS

The authors would like to thank the National Natural Science Foundation of China (21467023), National Undergraduate Training Programs for Innovation and Entrepreneurship (201510749001) and Ningxia Natural Science Foundation (NZ15020, NZ1637) for financial support.

REFERENCES

Alighardashi, A., Pons, M. N. & Poitier, O. 2008 Présence et devenir des médicaments dans les eaux usées urbaines, une analyse bibliographique. *Journal of Water Science* **21** (4), 413–426.

- Belaib, F., Azzedine, M., Boubeker, B. & Abdeslam-Hassen, M. 2014 Experimental study of oxytetracycline retention by adsorption onto polyaniline coated peanut shells. *International Journal of Hydrogen Energy* **39** (3), 1511–1515.
- Brigante, M. & Schulz, P. C. 2011 Removal of the antibiotic tetracycline by titania and titania-silica composed materials. *Journal of Hazardous Materials* **192** (3), 1597–1608.
- Chen, C. 2008 Study on adsorption properties of activated sludge in dye wastewater treatment. Master thesis, Harbin Institute of Technology, Harbin, China.
- Chen, S. H. 2012 Study on the modification of corn stalks and its adsorption properties of hexavalent chromium ion. PhD thesis, Shandong University, Jinan, China.
- Chen, J. P. & Yang, L. 2006 Study of a heavy metal biosorption onto raw and chemically modified *Sargassum* sp. via spectroscopic and modeling analysis. *Langmuir* **22** (21), 8906–8914.
- Choi, K. J., Kim, S. G. & Kim, S. H. 2008 Removal of tetracycline and sulfonamide classes of antibiotic compound by powdered activated carbon. *Environmental Technology* **29** (3), 333–342.
- Daghrir, R. & Drogui, P. 2013 Tetracycline antibiotics in the environment: a review. *Environmental Chemistry Letters* **11**, 209–227.
- Fathima, N. N., Aravindhan, R., Rao, J. R. & Nair, B. U. 2008 Dye house wastewater treatment through advanced oxidation process using Cu-exchanged Y zeolite: a heterogeneous catalytic approach. *Chemosphere* **70** (6), 1146–1151.
- Ho, Y. S. & McKay, G. 1999 Pseudo-second order model for sorption processes. *Process Biochemistry* **34**, 451–465.
- Homem, V. & Santos, L. 2011 Degradation and removal methods of antibiotics from aqueous matrices—a review. *Journal of Environmental Management* **92** (10), 2304–2347.
- Jia, M. Y., Wang, F., Bian, Y. R., Jin, X., Song, Y., Kengara, F. O., Xu, R. K. & Jiang, X. 2013 Effects of pH and metal ions on oxytetracycline sorption to maize-straw-derived biochar. *Bioresource Technology* **136**, 87–93.
- Jiang, T. S., Qi, L. W., Ji, M. R., Ding, H. H., Li, Y. H., Tao, Z. F. & Zhao, Q. 2012 Characterization of Y/MCM-41 composite molecular sieve with high stability from Kaolin and its catalytic property. *Applied Clay Science* **62–63**, 32–40.
- Jin, L., Amaya-Mazo, X., Apel, M. E., Sankisa, S. S., Johnson, E., Zbyszynska, M. A. & Han, A. 2007 Ca²⁺ and Mg²⁺ bind tetracycline with distinct stoichiometries and linked deprotonation. *Biophysical Chemistry* **128** (2–3), 185–196.
- Khan, A. A. & Singh, R. P. 1987 Adsorption thermodynamics of carbofuran on Sn(IV) arsenosilicate in H⁺, Na⁺ and Ca²⁺ forms. *Colloids and Surfaces* **24**, 33–42.
- Li, K., Yediler, A., Yang, M., Schulte-Hostede, S. & Wong, M. H. 2008 Ozonation of oxytetracycline and toxicological assessment of its oxidation by-products. *Chemosphere* **72** (3), 473–478.
- Li, X. C., Qi, J. Q., Jiang, R. X. & Li, J. 2016 Adsorptive Removal of As(III) from Aqueous Solution by Waste Litchi Pericarps. *Water Science and Technology* **74**, 2135–2144.
- Liu, M. M., Hou, L. A., Yu, S. L., Xi, B. D., Zhao, Y. & Xia, X. F. 2013 MCM-41 impregnated with A zeolite precursor: synthesis, characterization and tetracycline antibiotics removal from aqueous solution. *Chemical Engineering Journal* **223**, 678–687.

- Liu, T., Chang, B. & Ma, C. 2014 Simultaneous adsorption of oxytetracycline and copper(II) onto loess soil: kinetics properties and the effects of pH. *Advanced Materials Research* **838–841**, 976–980.
- Locatelli, M. A. F., Sodr , F. F. & Jardim, W. F. 2011 Determination of antibiotics in Brazilian surface waters using liquid chromatography-electrospray tandem mass spectrometry. *Archives of Environmental Contamination and Toxicology* **60** (3), 385–393.
- MacKay, A. A. & Canterbury, B. 2005 Oxytetracycline sorption to organic matter by metal-bridging. *Journal of Environmental Quality* **34** (6), 1964–1971.
- Mili , N., Milanovi , M., Letic, N. G., Sekuli , M. T., Radoni , J., Mihajlovi , I. & Miloradov, M. V. 2013 Occurrence of antibiotics as emerging contaminant substances in aquatic environment. *International Journal of Environmental Health Research* **23** (4), 296–310.
- Paul, T., Miller, P. L. & Strathmann, T. J. 2007 Visible-light-mediated TiO₂ photocatalysis of fluoroquinolone antibacterial agents. *Environmental Science & Technology* **41** (13), 4720–4727.
- Pereira, J. H. O. S., Vilar, V. J. P., Borges, M. T., Gonz lez, O., Espugas, S. & Boaventura, R. A. R. 2011 Photocatalytic degradation of oxytetracycline using TiO₂ under natural and simulated solar radiation. *Solar Energy* **85** (11), 2732–2740.
- Raji, C. & Anirudhan, T. S. 1998 Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. *Water Research* **32** (12), 3772–3780.
- Salama, T. M., Ahmed, A. H. & El-Bahy, Z. M. 2006 Y-type zeolite-encapsulated copper(II) salicylidene-p-aminobenzoic Schiff base complex: synthesis, characterization and carbon monoxide adsorption. *Microporous and Mesoporous Materials* **89** (1–3), 251–259.
- Wang, Y. J., Jia, D. A., Sun, R. J., Zhu, H. W. & Zhou, D. M. 2008 Adsorption and cosorption of tetracycline and copper(II) on montmorillonite as affected by solution pH. *Environmental Science & Technology* **42**, 3254–3259.
- Wang, L., Zhang, J., Zhao, R., Li, Y., Li, C. & Zhang, C. 2010 Adsorption of Pb(II) on activated carbon prepared from *Polygonum orientale* Linn: kinetics, isotherms, pH, and ionic strength studies. *Bioresource Technology* **101** (15), 5808–5814.
- Wang, D. S., Chao, Y. & Zhang, T. 2014 Adsorption Character of oxytetracycline and effect of pH on adsorption of oxytetracycline in soil. In: *The 6th International Conference on Environmental and Engineering Geophysics*, Jun 19–22, Chang'an University, Xi'an, China.
- Watkinson, A. J., Murby, E. J., Kolpin, D. W. & Costanzo, S. D. 2009 The occurrence of antibiotics in an urban watershed: from wastewater to drinking water. *Science of the Total Environment* **407** (8), 2711–2723.
- Xu, D. O. 2011 Preparation and investigation on properties of hierarchical porous nano-molecular sieves. PhD thesis, Jilin University, Changchun, China.
- Yousef, R. I., El-Eswed, B. & Al-Muhtaseb, A. H. 2011 Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: kinetics, mechanism, and thermodynamics studies. *Chemical Engineering Journal* **171** (3), 1143–1149.
- Zhang, Y., Cai, X. Y., Xiong, W. N., Jiang, H., Zhao, H. T., Yang, X. H., Li, C., Fu, Z. Q. & Chen, J. W. 2014 Molecular insights into the pH-dependent adsorption and removal of ionizable antibiotic oxytetracycline by adsorbent cyclodextrin polymers. *PLoS ONE* **9**, e86228.
- Zhao, C., Deng, H. P., Li, Y. & Liu, Z. Z. 2010 Photodegradation of oxytetracycline in aqueous by 5A and 13X loaded with TiO₂ under UV irradiation. *Journal of Hazardous Materials* **176**, 884–892.
- Zhao, C., Zhou, Y., de Ridder, D. J., Zhai, J., Wei, Y. M. & Deng, H. P. 2014 Advantages of TiO₂/5A composite catalyst for photocatalytic degradation of antibiotic oxytetracycline in aqueous solution: comparison between TiO₂ and TiO₂/5A composite system. *Chemical Engineering Journal* **248**, 280–289.

First received 5 September 2016; accepted in revised form 8 December 2016. Available online 27 December 2016