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Effects of loading metal ions on antibiotics adsorption by clay-sulfonated solid acid

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ABSTRACT

This study aims to explore the effect of loading metal ions on antibiotics adsorption by clay-based sulfonated solid acid. Bentonite (B) was continuously modified with nitric acid (N) and sulfuric acid (S) to obtain bentonite-based solid acid (NB) and sulfonated NB (SNB). SNB was loaded with Fe^{2+}, Cu^{2+}, and Mn^{2+} to obtain Fe-loaded SNB (Fe-SNB), Cu-loaded SNB (Cu-SNB), and Mn-loaded SNB (Mn-SNB). The thermodynamics and kinetics characteristics of the adsorption of tetracycline (TC), oxytetracycline (OTC), and chlortetracycline (CTC) on the tested materials were studied by batch method. The effects of environmental factors such as pH, temperature, and ionic strength on antibiotics adsorption were analyzed. Results showed that: (1) the adsorption isotherms of TC, OTC, and CTC were all suitable for the Langmuir equation, and the adsorption process was single-layer adsorption. Compared with SNB, the adsorption of antibiotics on metal ion-loaded SNB increased, and the increasing range followed the trend of Mn-SNB > Cu-SNB > Fe-SNB. The maximum adsorption capacity (q_m) of three antibiotics by the tested materials increased from 7.30 to 46.18 mol/kg, and the q_m of CTC was higher than that of TC and OTC. (2) The adsorption of TC, OTC, and CTC by each tested material conformed to the pseudo-second-order kinetics equation. High temperature benefitted the antibiotics adsorption by the tested materials, and the adsorption was a spontaneous, endothermic, and entropy-increasing process. (3) The adsorption capacity of antibiotics on the tested materials increased first and then decreased with increasing ionic strength and reached the maximum value of 0.1 mol/L. Increasing pH was not conducive to the adsorption of antibiotics, and specific surface area was the key to determine the adsorption effect.

Keywords: Bentonite; Sulfonated solid acid; Antibiotics; Adsorption capacity

1. Introduction

Antibiotics are biological products that have antibacterial, bactericidal, and antibacterial functions to varying degrees [1,2]. Antibiotics are widely used in large-scale animal breeding to prevent and treat diseases, improve feed utilization rate, and promote animal growth [3]. According to statistics, about 10 million tons of antibiotics and chemically synthesized antibiotics are used as veterinary drugs or feed additives in the breeding industry every year [4].

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Studies showed that about 30%–90% of antibiotics for animal use are excreted in animal feces in the form of drug precursor or metabolite [5]. Animal manure is eventually applied to the soil in the form of organic fertilizer. Part of antibiotics will be degraded or converted into harmless substances, while another part will be absorbed by the soil and exist in the soil environment for a long time, resulting in a long-term and far-reaching impact on the soil environment [6]. At present, rapid development of aquaculture in China has contributed to antibiotics pollution that poses serious threat to agricultural production; thus, the remediation and treatment of antibiotic pollution has become a hot spot for scientists all over the world [7].

In recent years, material adsorption has become a major subject of interest in pollution remediation research because of its simple operation, low cost, and obvious effects [8,9]. Bentonite (B) is an interlaminar silicate clay and mainly contains montmorillonite, which has been widely used in environmental remediation, catalysis and other fields [10]. Permanent negative charge and large internal and external surface area determine the high ion exchange capacity and strong adsorption capacity of B [11]. Liu [12] found that the adsorption effect of acid-modified B on antibiotics was better than that of original B, and hydrophobicity was one of the main mechanisms of the adsorption removal of antibiotics [13]. Wang et al. [14] used the amphoteric agent octadecyl dimethyl betaine (BS-18) to modify B for tetracycline (TC) adsorption; the adsorption amount of TC by BS-18-modified B was mainly due to charge attraction. Sulfonic acid groups on carriers (molecular sieve, alumina, silica, etc.) have sulfonic acid characteristics [15]. Solid acid has a large surface area, pore volume, and high adsorption capacity to pollutants [16].

Metal ion loading can produce materials with the advantages of large specific surface areas, good pore structures, and abundant surface active functional groups; it plays an important role in the adsorption of organic and inorganic pollutants in the environment [17,18]. Ding et al. [19] reported that manganese oxide-modified diatomite exhibited good removal effect on Cr^{6+} in water and excellent adsorption performance under strong acidic conditions, with removal rate up to 96%. The adsorption capacity of coated clay with iron oxide for Cr(VI) was greatly enhanced compared with that of the original soil [20]. The maximum adsorption capacity for 2-chlorophenol by Cu-nano loaded zeolite was 204.68 mg/g at optimum pH 6.0 with 150 min of reaction time [21]. The loading of metal ions and the acid modification of materials can improve the ability of the materials to adsorb pollutants, if metal ions are loaded again on acid-modified clay, then the adsorption capacity of the composite-acid modified clay for pollutants will be greatly enhanced. However, reports on the adsorption of pollutants on acid-modified clay loaded by metal ions are few.

In this work, clay-based sulfonated solid acid was loaded by Fe^{2+}, Cu^{2+}, and Mn^{2+} as an adsorbent for removal of TC, oxytetracycline (OTC), and chlortetracycline (CTC). The adsorption thermodynamics and kinetics characteristics of antibiotics were studied. The effects of environmental factors such as temperature, pH, and ionic strength on adsorption performance were compared. Results provide a theoretical basis for using clay-based materials for pollution control and remediation of soils containing antibiotics.

2. Materials and method

2.1. Experimental materials

The test clay was sodium B (Meishan City, Sichuan Province, particle-size of 400 mesh). Nitric acid (HNO_3, AR), sulfuric acid (H_2SO_4, AR), ferrous sulfate heptahydrate ($FeSO_4·7H_2O$, AR), manganese sulfate monohydrate ($MnSO_4·H_2O$, AR), and copper sulfate pentahydrate ($CuSO_4·5H_2O$, AR) were purchased from Chengdu Cologne Chemical Co., Ltd., China. TC, OTC, and CTC with purity of more than 99% were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd., China.

2.1.1. Preparation of bentonite-based solid acid

Appropriate amount of sodium B was weighed in a 250 mL container, placed in oven for drying and added with a certain volume of HNO_3 solution with a mass fraction of 68% (the volume covered with bentonite so that it could be fully mixed). The stopper was placed in a thermostatic oscillator at 25°C for 8 h and centrifuged (4,000 rpm) for 10 min. The separated sample was repeatedly washed with deionized water (dH_2O) until the filtrate was neutral (pH = 7). Finally, bentonite-based solid acid (NB) was dried at 60°C to constant weight, cooled to room temperature, and ground through a 100-mesh sieve.

2.1.2. Preparation of sulfonated NB

NB was sulfonated with concentrated sulfuric acid (>98 wt.%) at 130°C for 60 min in the reaction flask after drying in oven, with m (NB, g) : V (concentrated sulfuric acid, mL) = 1:5. After natural cooling to room temperature, the flask was centrifuged (4,000 r/min) for 10 min. The separated sample was repeatedly washed with dH_2O until the filtrate was neutral (pH = 7). Finally, the sample was dried at 60°C to constant weight and ground through a 100-mesh sieve after cooling to room temperature to obtain sulfonated NB (SNB).

2.1.3. Preparation of metal ion-loaded SNB

A certain amount of SNB was weighed and added to the prepared solutions of $FeSO_4·7H_2O$, $CuSO_4·5H_2O$, and $MnSO_4·H_2O$. The mass ratio of metal ions to SNB was 0.2, the solid–liquid ratio was 1:10, and the temperature was 25°C. After ultrasonic oscillation at 100 Hz for 2 h, the sample was centrifuged (4,000 rpm) for 15 min. The separated metal ion-loaded SNB was washed with dH_2O repeatedly, calcined in muffle furnace at 300°C for 1 h, cooled to room temperature, and ground through 100-mesh sieve. Three kinds of metal ion-loaded SNB were obtained and labeled Fe-loaded SNB (Fe-SNB), Cu-loaded SNB (Cu-SNB), and Mn-loaded SNB (Mn-SNB), respectively. The basic physico-chemical properties of the tested samples are shown in Table 1.

Table 1
Physico-chemical properties of the tested samples

Tested sample	pH	Cation exchange capacity (mmol/kg)	Specific surface area (m^2/g)
B	9.97	1,121.44	63.34
NB	6.22	1,152.23	66.30
SNB	5.77	1,101.42	67.65
Fe-SNB	7.44	1,201.92	72.42
Cu-SNB	7.39	1,212.18	73.53
Mn-SNB	7.13	1,276.01	82.35

2.2. Experimental design

2.2.1. Adsorption isotherms of antibiotics

The concentrations of TC were set at nine concentration gradients of 0.5, 1, 2, 5, 10, 20, 30, 40, and 50 mg/L, while OTC and CTC were set at nine concentration gradients of 0.3, 0.6, 1.2, 3, 6, 12, 18, 24, and 30 mg/L. The temperature was set at 25°C, the pH value of the solution was set as 4, and the ionic strength was set as 0.1 mol/L NaCl.

2.2.2. Kinetics adsorption of antibiotics

The concentrations of TC was 50 mg/L, and the concentrations of OTC and CTC were 30 mg/L. The adsorption time was set as 5, 10, 30, 60, 120, 180, 240, 300, 360, 480, 600, and 720 min. The temperature was set as 25°C, the pH value of the solution was set as 4, and the ionic strength was set as 0.1 mol/L NaCl.

2.2.3. Influence of environmental factors

The initial pH values of the solution were set as 2, 4, 6, 8, and 10; the solution temperature was set as 25°C; and the ionic strength was set as 0.1 mol/L NaCl. The experimental temperatures were set at 25°C, 35°C, and 40°C; the pH of the solution was set at 4; and the ionic strength was set at 0.1 mol/L NaCl. The initial ionic strength of the solution was set to 0.05, 0.1, and 0.5 mol/L NaCl; the solution temperature was set to 25°C; and the pH value was set to 4.

2.3. Experimental methods

Batch equilibrium method was used for antibiotic adsorption. A total of 0.5000 g of the sample was weighed in nine 50 mL plastic centrifuge tubes and added with 20 mL of antibiotic solutions with different concentration gradients. The samples were oscillated at 25°C and 200 rpm for 12 h at constant temperature [11] and centrifuged at 4,800 rpm for 10 min. The concentration of antibiotics in the supernatant was determined, and the equilibrium adsorption amount was calculated by subtraction method. All the above measurements were inserted into standard solution for analytical quality control.

2.4. Data processing

2.4.1. Calculation of equilibrium adsorption capacity

The equilibrium adsorption capacity can be calculated according to Eq. (1):

$$q=\frac{\left(C_0-C_e\right)V}{m} \tag{1}$$

where V is the volume of solution (mL); c_0 is the antibiotic concentration at the starting point (mmol/L); c_e is the antibiotic concentration at the equilibrium point (mmol/L); m is the mass of tested sample (g); and q is the equilibrium adsorption capacity of tested sample for antibiotics (mol/kg).

2.4.2. Fitting of adsorption isotherms

The Langmuir model [22] was selected to fit the adsorption isotherms of the three antibiotics according to the adsorption isotherm trend. Eq. (2) was expressed as follows:

$$q=\frac{q_m bc}{1+bc} \tag{2}$$

where q is the equilibrium adsorption amount of antibiotics for the amended soil, mol/kg; c is the equilibrium concentration of antibiotics in the solution, mol/kg; q_m is the maximum adsorption amount of antibiotics for the tested sample, mol/kg; and b is the apparent equilibrium constant of antibiotic adsorption on the tested sample for the measurement of adsorption affinity.

2.4.3. Fitting of adsorption kinetics model

The pseudo-first-order and pseudo-second-order kinetics equation models were used to simulate the adsorption process of three antibiotics on different modified materials [23]. The kinetics equations were defined as Eqs. (3) and (4).

$$\ln\left(q_e-q_t\right)=\ln q_e-k_1t \tag{3}$$

$$\frac{t}{q_t}=\frac{1}{q_e^2k_2}+\frac{t}{q_e} \tag{4}$$

where q_t is the adsorption capacity corresponding to the adsorbent at time t (mol/kg); q_e is the equilibrium adsorption capacity of tested sample for antibiotics (mol/kg); k_1 and k_2 are pseudo-first-order and pseudo-second-order reaction rate constants respectively; t is the adsorption time (min).

2.4.4. Calculation of thermodynamic parameters

Parameter b in the Langmuir model is equivalent to the apparent adsorption constant of equilibrium constant, and the thermodynamic parameter calculated by $b = K$ or K_a was called the apparent thermodynamic parameter [14]. Eqs. (5)–(7) were defined as follows:

$$\Delta G=-RT\ln K \tag{5}$$

$$\Delta S=\frac{\Delta H-\Delta G}{T} \tag{6}$$

$$\Delta H = R\left(\frac{T_1 \cdot T_2}{T_2 - T_1}\right) \cdot \ln\left[\frac{K_a, T_2}{K_a, T_1}\right] \tag{7}$$

where ΔG is the standard free energy change (kJ/mol), R is a constant (8.3145 J/mol·K), T is the adsorption temperature (T_1 = 293.16 K and T_2 = 313.6 K), ΔH is the enthalpy of adsorption process (kJ/mol), and ΔS is the entropy change of adsorption process (J/mol·K).

CurveExpert 1.4 fitting software was used in isothermal fitting, and Origin 9.0 was adopted to improve data plotting. SPSS 16.0 statistical analysis software was used to process the experimental data for variance and correlation analysis.

3. Results and discussion

3.1. Adsorption isotherms of antibiotics by different tested materials

The adsorption isotherms of TC, OTC, and CTC by different tested materials are shown in Fig. 1. The adsorption capacity of TC, OTC, and CTC on the tested materials increased with increasing equilibrium concentration and showed an "L" type pattern. The adsorption parameters fitted by the Langmuir model (Table 2) showed that the correlation coefficients reached extremely significant level (P = 0.01) indicating that the adsorption of TC, OTC, and CTC by the tested materials conformed to the Langmuir model and was mainly monolayer adsorption.

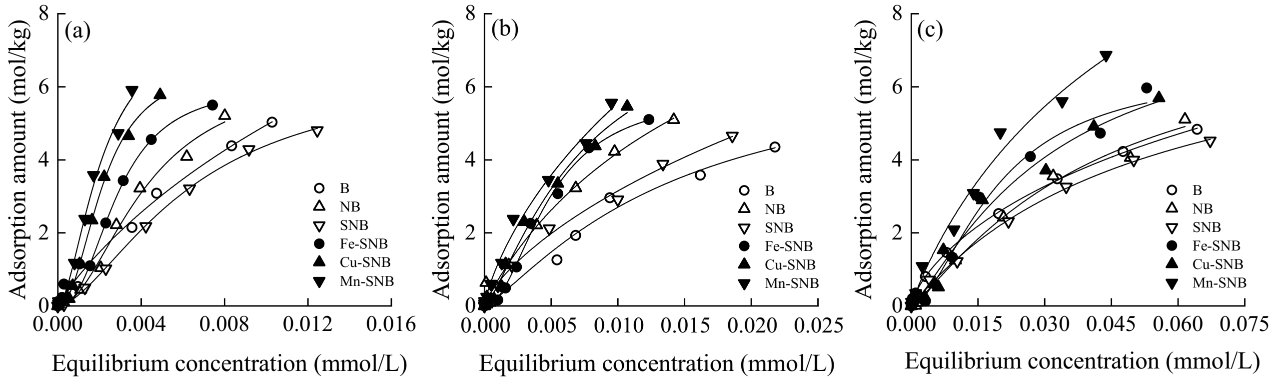

Fig. 1. Adsorption isotherms of TC (a), OTC (b), and CTC (c) on different tested materials.

Table 2
Fitting parameters of TC, OTC, and CTC adsorption by the Langmuir model

Treatments		Fitting parameters			
		Correlation coefficient (r)	Standard deviation (S)	q_m (mol/kg)	b (L/mol)
TC	B	0.9995**	0.11	7.30	29.03
	NB	0.9911**	0.16	11.09	13.23
	SNB	0.9974**	0.07	8.36	17.90
	Fe-SNB	0.9814**	0.33	13.02	15.30
	Cu-SNB	0.9757**	0.29	12.32	15.58
	Mn-SNB	0.9836**	0.39	17.30	15.05
OTC	B	0.9922**	0.14	8.38	63.46
	NB	0.9875**	0.32	12.42	25.37
	SNB	0.9942**	0.35	16.91	39.93
	Fe-SNB	0.9796**	0.19	10.11	115.79
	Cu-SNB	0.9835**	0.20	10.52	66.84
	Mn-SNB	0.9889**	0.21	17.31	42.60
CTC	B	0.9896**	0.20	9.01	104.15
	NB	0.9877**	0.35	9.79	77.39
	SNB	0.9970**	0.28	15.42	46.72
	Fe-SNB	0.9845**	0.31	14.58	87.19
	Cu-SNB	0.9971**	0.35	34.38	43.18
	Mn-SNB	0.9910**	0.26	46.18	41.12

Note: **means significant correlation at P = 0.01 level.

The maximum adsorption capacity (q_m) of the tested materials for antibiotics was increased from 7.30 to 46.18 mol/kg and presented the order of OTC = TC < CTC, consistent with the results shown by adsorption isotherm in Fig. 1. The adsorption amounts of NB and SNB for antibiotics increased compared with that of B. After loading with the metal ions, the adsorption capacity of SNB to the antibiotics was further improved and had best adsorption effect on Mn-SNB. The adsorption amounts of Fe-SNB, Cu-SNB, and Mn-SNB for the antibiotics were 1.21–1.78, 1.25–3.82 and 2.07–5.13 times higher than that of B, respectively. B had a high specific surface area and abundant surface adsorption sites and formed a weak ion exchange effect on the antibiotics. After modification with N and S, the negative charge points of B increased; thus, the q_m of the antibiotics in NB and SNB was higher than that of B [24]. After loading by metal ions, the specific surface area and surface adsorption sites of NB and SNB improved, and the adsorption capacity of the antibiotics by Fe-SNB, Cu-SNB, and Mn-BS-B increased [22]. Mn-BS-B used in water improvement had a high adsorption capacity for antibiotics and is thus a suitable material.

3.2. Adsorption kinetic characteristics of antibiotics by different tested materials

The adsorption kinetics curve of TC, OTC, and CTC on different tested materials are shown in Fig. 2. The adsorption equilibrium of TC and CTC was reached at about 120 min, and that of OTC was reached at 180 min. The pseudo-first-order and pseudo-second-order kinetics equation models were used to simulate the adsorption process of

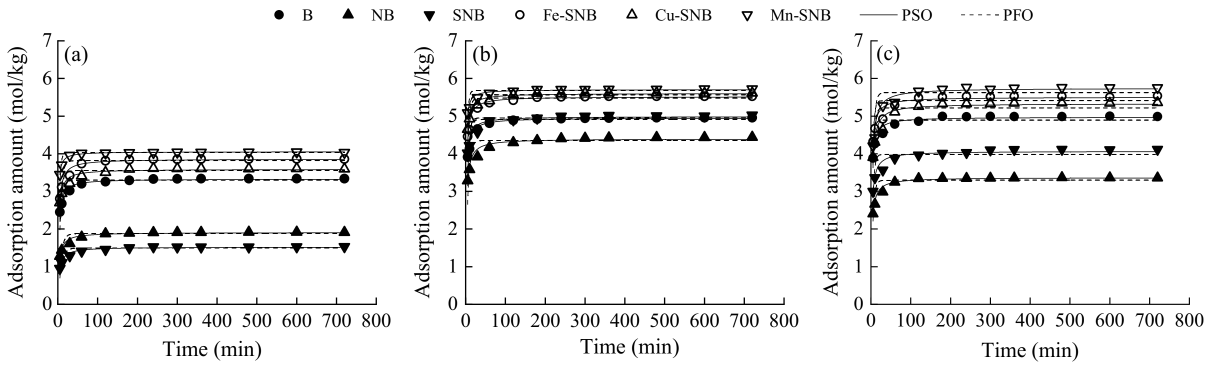

Fig. 2. Adsorption kinetics of TC (a), OTC (b), and CTC (c) on different tested materials.

Table 3
Fitting parameters of adsorption kinetics for TC, OTC, and CTC

Treatments		Pseudo-first-order kinetic equation			Pseudo-second-order kinetic equation		
		q_e (mol/kg)	k_1 (min^{-1})	R^2	q_e (mol/kg)	k_2 (kg/mol·min)	R^2
TC	B	3.30	0.1836	0.7282	3.33	0.1459	0.9702
	NB	3.55	0.1939	0.7190	3.59	0.1469	0.9461
	SNB	1.50	0.1257	0.7840	1.52	0.1892	0.9694
	Fe-SNB	3.82	0.1792	0.7321	3.86	0.1214	0.9634
	Cu-SNB	4.03	0.3042	0.6301	4.05	0.2781	0.9959
	Mn-SNB	1.88	0.1425	0.7668	1.91	0.1782	0.9520
OTC	B	5.22	0.2380	0.7349	5.33	0.0883	0.9379
	NB	3.30	0.2232	0.7940	3.37	0.1305	0.9668
	SNB	3.98	0.2478	0.7378	4.07	0.1232	0.9347
	Fe-SNB	5.41	0.2861	0.6939	5.50	0.1156	0.9240
	Cu-SNB	5.62	0.2257	0.7491	5.74	0.0784	0.9461
	Mn-SNB	4.89	0.2852	0.7586	4.97	0.1303	0.9563
CTC	B	5.47	0.2352	0.6838	5.52	0.1298	0.9506
	NB	4.35	0.1890	0.7234	4.40	0.1153	0.9449
	SNB	5.68	0.3447	0.6011	5.70	0.2526	0.9419
	Fe-SNB	4.91	0.2229	0.6941	4.95	0.1324	0.9662
	Cu-SNB	4.95	0.2322	0.6863	4.99	0.1405	0.9327
	Mn-SNB	5.57	0.2644	0.6603	5.60	0.1560	0.9615

antibiotics on the tested materials. The fitting parameters of adsorption kinetics are shown in Table 3. The adsorption kinetics of different tested materials are consistent with the pseudo-second-order kinetics equation. The R^2 values of the pseudo-second-order kinetics equation for TC, OTC, and CTC adsorption were 0.9461–0.9959, 0.9240–0.9668, and 0.9327–0.9662, respectively. Therefore, the pseudo-second-order kinetics equation model can accurately describe the adsorption dynamics. The adsorption rate of different tested materials was not directly proportional to the driving force but directly proportional to the square of the driving force. This adsorption rate was controlled by chemical adsorption mechanism [25], indicating that the adsorption of the antibiotics by the tested materials is mainly chemical adsorption.

3.3. Effect of temperature on adsorption of antibiotics

The influence of temperature on TC, OTC, and CTC adsorption by the tested materials is shown in Fig. 3. As the temperature increased from 25°C to 45°C, the adsorption amount of the tested materials for the antibiotics increased with increasing temperature, indicating that the active site of the tested materials was more strongly bound to the antibiotics at high temperatures and presenting a positive warming effect [3]. The adsorption amounts of Fe-SNB, Cu-SNB, and Mn-SNB for TC were increased by 9.65%, 1.60%, and 8.09% from 25°C to 45°C. With increasing temperature, the antibiotic molecular diffusion rate in the solution and the contact between the antibiotics and the surface of the materials increased.

Table 4 shows the thermodynamic parameters of TC, OTC, and CTC adsorption by the tested materials. At 25°C and 45°C, the Gibbs free energy variation ΔG of antibiotics adsorption was negative, indicating that the adsorption was a spontaneous reaction. The enthalpy change ΔH of the tested materials was greater than zero, indicating that the adsorption was an endothermic reaction. The increase in temperature would increase the thermal process of antibiotics and promote the chemisorption process. This result mutually supported the conclusion that increasing temperature was beneficial to the adsorption of antibiotics (Fig. 3). The entropy change ΔS of the tested materials were all greater than zero, indicating that the adsorption belonged to entropy-increasing reaction; hence, the randomness of antibiotics molecules at the solid–liquid interface increased during the adsorption process [22].

3.4. Effect of pH and ionic strength on adsorption of antibiotics

Fig. 4 shows the influence of pH on TC, OTC, and CTC adsorption by different tested materials. With increasing pH, the adsorption amount of the tested materials for antibiotics decreased. The increase amplitudes of the antibiotics adsorbed by the tested samples were 28.97%–58.94% (TC), 18.50%–62.24% (OTC), and 41.95%–81.03% (CTC). The pH of the solution had a great influence on the adsorption effect of the tested materials, which may be related to the existence of tetracycline antibiotics in aqueous solution. Three ionizable groups were found in the molecular structures of the antibiotics, and the ionization equilibrium constants $\mathrm{p}K_{\mathrm{a1}}$, $\mathrm{p}K_{\mathrm{a2}}$, and $\mathrm{p}K_{\mathrm{a3}}$ were 3.30–3.57, 7.49–7.69, and 9.44–9.88, respectively. Antibiotics with pH < 3.30 is positively charged, that with pH between 3.30 and 7.69 is positively or negatively charged, and that with pH > 9.50 exists as an anion [26]. Therefore, under acidic conditions, antibiotics can

Table 4
Thermodynamics parameters of TC, OTC, and CTC on the tested materials

Treatments		ΔG (kJ/mol)		ΔH (kJ/mol)	ΔS (J/mol·K)
		25°C	45°C		
TC	B	–8.35	–9.27	5.40	46.11
	NB	–6.40	–7.26	6.42	43.01
	SNB	–7.15	–8.69	15.83	77.07
	Fe-SNB	–6.76	–7.48	3.99	36.07
	Cu-SNB	–6.81	–7.31	0.63	24.94
	Mn-SNB	–6.72	–7.40	3.34	33.74
OTC	B	–9.14	–9.92	2.50	39.03
	NB	–9.30	–10.15	3.32	42.32
	SNB	–10.29	–11.54	8.38	62.60
	Fe-SNB	–11.78	–12.83	3.93	52.70
	Cu-SNB	–10.42	–11.42	4.52	50.08
	Mn-SNB	–8.02	–8.82	3.96	40.17
CTC	B	–11.08	–12.01	2.89	46.83
	NB	–10.78	–12.56	15.77	89.04
	SNB	–9.53	–10.60	6.39	53.39
	Fe-SNB	–11.52	–12.57	4.25	52.87
	Cu-SNB	–9.33	–10.20	3.62	43.44
	Mn-SNB	–9.21	–9.95	1.79	36.90

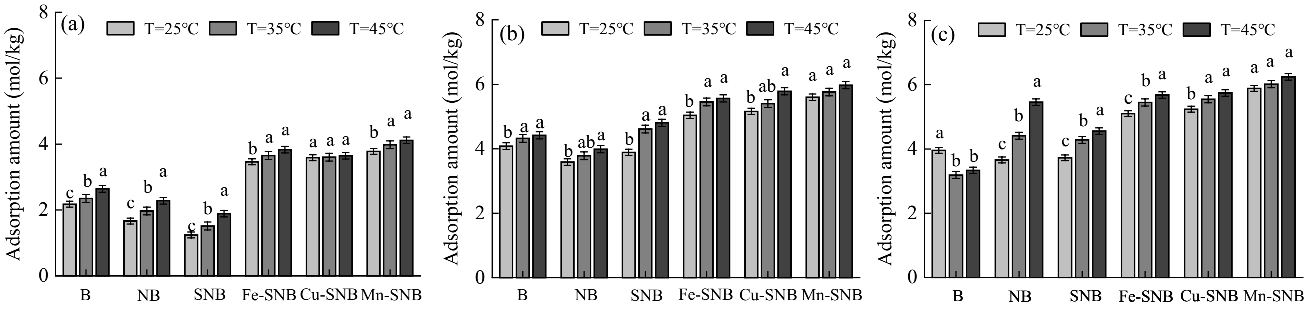

Fig. 3. Effect of temperature on the adsorption of TC (a), OTC (b), and CTC (c).

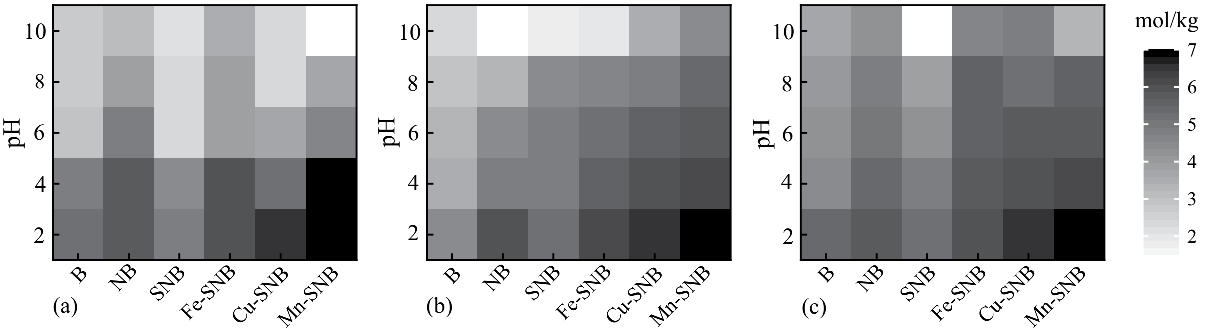

Fig. 4. Effect of pH on the adsorption of TC (a), OTC (b), and CTC (c).

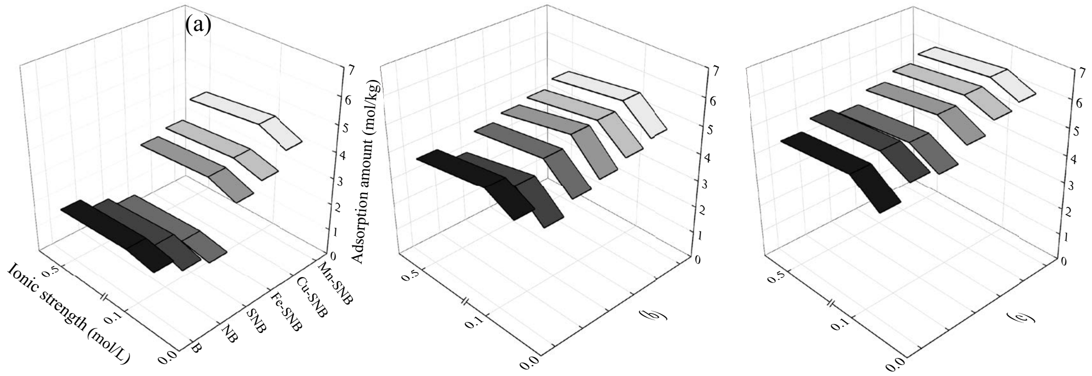

Fig. 5. Effect of ionic strength on the adsorption of TC (a), OTC (b), and CTC (c).

be combined with the negative charge on the surface of the tested materials by cation exchange, thereby increasing the adsorption. With increasing pH, the proportion of negative charge in the antibiotics molecule increased and the adsorption decreased gradually [12].

Fig. 5 shows the influence of ionic strength on the adsorption of TC, OTC, and CTC by the tested materials. With increasing ionic strength, the adsorption amount of the tested materials for antibiotics increased first and then decreased, reaching the maximum at 0.1 mol/L. When the ionic strength increased from 0.05 to 0.1 mol/L, the adsorption amount of the antibiotics on the tested materials was increased by 8.99%–19.26% (TC), 12.63%–27.58% (OTC), and 6.81%–16.98% (CTC), respectively. The results may be due to the enhancement of the hydrophobic performance of antibiotic molecules. Low Na^+ concentration in the solution enhanced the solubility of antibiotics. When the ionic strength was increased from 0.1 to 0.5 mol/L, the concentration of Na^+ in the solution was high, the antibiotic molecules were not easily released, and the solubility of the antibiotics decreased [27].

3.5. Effect of physico-chemical properties on antibiotic adsorption

The q_m values of TC, OTC, and CTC of the tested materials were linearly fitted with their physico-chemical properties, and the fitting results are shown in Table 5. Negative correlations were found between pH and q_m of TC, OTC, and CTC, and positively correlations were detected between cation exchange capacity (CEC), specific surface area (S_{BET}), and q_m of TC, OTC, and CTC. CEC and S_{BET} all had significant correlation with the q_m of TC and CTC and had low or moderate correlation with the q_m of OTC. Hence, S_{BET} is the key to determine the adsorption effect of antibiotics by the tested materials. The increase in S_{BET} could increase the contact opportunities between the antibiotics and materials, thereby increasing their adsorption capacity.

Table 5
Relationship between q_m and physico-chemical properties of the tested materials

Antibiotic	Regression equation	Correlation coefficients (r)	Standard deviations (S)
TC	$q_m = 16.14 - 0.62pH$	0.2546	3.88
	$q_m = -51.11 + 0.05CEC$	0.9638**	1.07
	$q_m = -23.93 + 0.50S_{BET}$	0.9451**	1.31
OTC	$q_m = 25.62 - 1.78pH$	0.6991	2.97
	$q_m = -1.04 + 0.01CEC$	0.2024	4.07
	$q_m = -7.01 + 0.28S_{BET}$	0.5036	3.59
CTC	$q_m = 32.11 - 1.44pH$	0.1388	16.81
	$q_m = -211.32 + 0.20CEC$	0.8455*	9.07
	$q_m = -125.13 + 2.07S_{BET}$	0.9220**	6.57

Notes: **and *respectively indicate significant correlation at the level of $P = 0.01$ and $P = 0.05$.

4. Conclusion

- The adsorption capacity of different tested materials for antibiotics was improved compared with that of B and presented the order of Mn-SNB > Cu-SNB and Fe-SNB. The pseudo-second-order kinetics equation model can accurately describe the adsorption process of TC, OTC, and CTC.
- The adsorption of TC, OTC, and CTC by the tested materials decreased with increasing pH, increased with increasing temperature, and increased first and then decreased with increasing ionic strength.
- The thermodynamics parameters show that the adsorption of the antibiotics by the tested materials was a spontaneous, endothermic and entropy-increasing process. S_{BET} is the key to determine the adsorption effect of the antibiotics.

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Conflict of interests

The authors declare that they have no conflict of interest.

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