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Performance comparison of Mg-loaded amphoteric clays in antibiotics adsorption from aqueous solutions

Wen-bin Li[a,b,†], Shu-ni Zhou[a,†], Hong-yan Deng[a,*], Abbas Touqeer[c]

[a]*College of Environmental Science and Engineering, China West Normal University, Nanchong Sichuan 637009, China, emails: dhongyan119@163.com (H.-y. Deng), 3234017295@qq.com (S.-n Zhou), lwb062@163.com (W.-b. Li)*
[b]*Institution of Environmental Science, China West Normal University, Nanchong, Sichuan 637002, China*
[c]*Department of Soil, Water, and Climate, University of Minnesota, Twin 637009, USA, email: abbastouqeer@yahoo.com (A. Touqeer)*

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ABSTRACT

To explore the adsorption performance of antibiotics in different amphoteric clays loaded with magnesium (Mg) and dodecyl dimethyl betaine (BS) was used to modify bentonite (B), kaolin (K), and diatomite (D) to obtain different amphoteric clays (named as BS-B, BS-K, and BS-D, respectively). Then, Mg-loaded amphotropic clays (abbreviated as Mg-BS-B, Mg-BS-K, and Mg-BS-D, respectively) were obtained by loading Mg ions on BS-B, BS-K, and BS-D. The isothermal adsorption characteristics of tetracycline (TC), chlortetracycline (CTC), and oxytetracycline (OTC) were studied by batch treatment with B, K, and D as the controls, and the adsorption differences under different environmental factors (i.e., temperature, pH, and ionic strength) were compared. The results show that the following. (1) The TC, CTC, and OTC adsorptions of the tested samples were all suitable for Langmuir isothermal adsorption model, and the maximum adsorption capacities (q_m) were 1.70–5.21 mol/kg (TC), 1.80–5.94 mol/kg (CTC), and 1.81–6.28 mol/kg (OTC). Under the same modification conditions, the q_m of TC, CTC, and OTC followed the order Mg-BS-B > Mg-BS-K > Mg-BS-D. (2) When the temperature changed from 25°C to 45°C, the adsorption amount of TC, CTC, and OTC on the tested samples increased, exhibiting a positive temperature effect. The thermodynamic parameters showed that the adsorption of TC, CTC, and OTC was spontaneous, endothermic, and entropic-_increasing processes. (3) In the pH range of 2–10, the adsorption amount of TC, CTC, and OTC on each soil sample increased first and then decreased and reached the peak value at pH = 6. With the increase of the ionic strength, the adsorption amount of the three antibiotics decreased, and the decrease ranges were 15.17%–84.17% (TC), 16.07%–68.07% (CTC) and 16.30%–76.54% (OTC).

Keywords: Amphoteric clay; Magnesium loading; Antibiotics; Adsorption amount

1. Introduction

With the continuous improvement of breeding industry, numerous antibiotics have been used in livestock and poultry in the pursuit of economic benefits, resulting in the abuse of antibiotics and a great threat to human health [1,2]. Tetracycline (TC), chlortetracycline (CTC), and oxytetracycline (OTC) are the most widely used antibiotics in current animal breeding. A large percentage of antibiotics cannot be completely absorbed by the animal body and enter the water environment in the form of protoforms or

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* Corresponding author.
[†] These authors have contributed equally to this work and share first authorship.

metabolites, resulting in the increasingly serious pollution of water [3,4]. The adsorption method has a strong application value in the field of water pollution remediation due to its advantages of simple operation, high removal efficiency, and low-cost [5,6]. Therefore, using adsorption materials for the remediation of antibiotics in wastewater has become a popular global issue.

The materials commonly used for antibiotics adsorption include carbonaceous materials (such as activated carbon, graphene, and biochar), metal-organic skeleton materials, natural clay minerals, resins, hydrogels, and molecular imprinted materials [7–9]. Clays are superior sorbents with unique structures, cheap, easy to obtain, and widely used in water treatment [10,11]. Maataoui et al. [12] found that the adsorption capacity of spiramycin antibiotics in aqueous solution by bentonite (B) is 260.3 mg/g, and the adsorption capacity decreases in the presence of NaCl. When Iraqi natural B is used to adsorb TC, 90% of the TC could be removed under optimal adsorption conditions, and the maximum adsorption capacity is 23.69 mg/g [13]. Studies show that the adsorption capacity of modified materials is stronger than that of unmodified materials [14,15]. The commonly used modified modifiers include cetyltrimethylammonium bromide, polyacrylamide, chitosan, polydimethyldiallyl ammonium chloride, organic acids, and metal ions [16]. The adsorption isotherms of TC on modified clay are consistent with the Henry model, and the adsorption amount of TC increases by 1.04–1.81 times [17,18]. Wang et al. [19] used an amphoteric surfactant (octadecyl dimethyl betaine) to modify B and found that the adsorption of TC by BS-18-modified B is mainly based on the charge and positively affected by the increasing temperatures.

Metal ion loading can produce materials with the advantages of large specific surface area, good pore structure, and abundant surface-active functional groups; this method plays an important role in the adsorption of the organic and inorganic pollutants in the environment [20,21]. The phosphorus adsorption capacity of MgO-loaded biochar is 110.29 mg/g. Compared with unmodified biochar, the phosphorus adsorption effect of modified biochar is significantly enhanced [22]. Fagundes et al. [23] used copper ion modified B to adsorb TC, and their results show that the modified B could remove 98.23% of TC in the solution. The loading of metal ions and the amphoteric modification of materials improve the ability of the materials to adsorb pollutants. If Mg ions are loaded again on the basis of the amphoteric modification of clay, the adsorption capacity of the Mg-loaded amphoteric clay for pollutants will be greatly enhanced. However, reports on the adsorption of pollutants on Mg-loaded amphoteric clay are few to date.

In this study, B, kaolin (K), and diatomite (D) were modified by an amphoteric modifier for preparing amphoteric clays. Then, the amphoteric clays were loaded with magnesium ion as an adsorbent for removal of TC, CTC, and OTC removal. The isothermal adsorption characteristics of TC, CTC, and OTC were studied. The effects of pH, temperature, and ionic strength on the adsorption performance were investigated. The results provide a theoretical reference for the application of water remediation technology in antibiotic pollution.

2. Materials and method

2.1. Experimental materials

Dodecyl dimethyl betaine (BS, Tianjin Xingguang Auxiliary Factory) was used as an amphoteric modifier. The molecular formula of BS is $C_{16}H_{33}NO_2$, and it has the following properties: pH of 6.5–7.5, solubility (20°C) of 160 g/100 g of water, and active substance content of 50% ± 2%. The tested clays with a particle size of 400 mesh were B, K, and D, which were purchased from Tongchuang Bentonite Company in Henan Province, Guangzhou Tuoyi Trading Co., Ltd., and Chengdu Cologne Chemical Reagent Factory, respectively. TC, CTC, and OTC with a purity of 99.9% were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Magnesium sulfate heptahydrate ($MgSO_4·7H_2O$, AR) was purchased from Chengdu Cologne Chemical Co., Ltd.

2.1.1. Preparation of amphoteric clay

A wet process was adopted to prepare BS-modified clay (BS-clay) [24]. In this process, 100 g of clay was slowly added to 1.0 L of dH_2O, and different ratios of BS, which were calculated in accordance with the cation exchange capacity (CEC) of clay, were added again. After stirring at 40°C for 3 h, the samples were separated, washed with dH_2O thrice, dried at 60°C for 12 h, and passed through a 60-mesh sieve. Next, BS-modified B, K, and D were prepared and recorded as BS-B, BS-K, and BS-D, respectively. The BS weight for a certain weight of clay can be obtained by using Eq. (1).

$$W = \frac{m \times \text{CEC} \times M \times 10^{-6} \times R}{b} \tag{1}$$

where W (g) refers to the weight of BS, m (g) refers the weight of the clay that will be modified, CEC (mmol/kg) represents the CEC of clay, M (g/mol) is the molecular mass of BS, R stands for the modified proportion of BS, and b specifies the product content of BS (mass fraction).

2.1.2. Preparation of Mg-loaded BS-clay

Approximately 30.00 g of BS-clay was dispersed in 4 mol/L sodium hydroxide (NaOH) solution with solid–liquid ratio of 1:3 and stirred in a water bath at constant temperature (90°C) at 150 rpm speed for 2 h. Then, 250 mL of 1 mol/L $MgSO_4·7H_2O$ solution was added to the mixture. The resulting solution was fully stirred for 1 h and left to stand at room temperature for 24 h, the sample was centrifuged (4,000 rpm) for 15 min, dried at 60°C for 12 h and passed through a 60-mesh sieve. Three kinds of Mg ion-loaded BS-clay were obtained and labeled Mg-BS-B, Mg-BS-K, and Mg-BS-D.

2.2. Experimental design

2.2.1. Isothermal adsorption experiment

The concentrations of TC, CTC, and OTC were set to nine concentration gradients of 0.5, 1, 2, 5, 10, 20, 30, 40, and 50 mg/L. The temperature was set to 25°C, the pH of the solution was set to 6, and the ionic strength was set to 0.1 mol/L of NaCl.

2.2.2. Influence factor experiment

The temperature, the pH, and the ionic strength were considered.

The experimental temperature was set to 25°C, 35°C, and 45°C (the pH of the solution was set to 6, and the ionic strength was set to 0.1 mol/L NaCl). The pH of the contaminated solution was set as 2, 4, 6, 8, and 10 (the solution temperature was set as 25°C, and the ionic strength of the solution was set as 0.1 mol/L NaCl). The ionic strength was set to 0.01, 0.1, and 0.5 mol/L (the solution temperature was set to 25°C, and the pH value was set to 6).

2.3. Experimental methods

The 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 to which 20 mL of antibiotic solutions with different concentration gradients were respectively added. The samples were oscillated at 25°C and 200 rpm for 12 h at constant temperature [25] and centrifuged at 4,800 rpm for 10 min. The concentration of the antibiotics in the supernatant was determined, and the equilibrium adsorption amount was calculated by the subtraction method. All the above measurements were substituted into the standard solution for analytical quality control.

2.4. Data processing

2.4.1. Fitting of adsorption isotherms

The Langmuir model [26] 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 the antibiotic adsorption on the tested sample for the measurement of adsorption affinity.

2.4.2. Calculation of thermodynamic parameters

Parameter b in the Langmuir model is equivalent to the apparent adsorption constant of the equilibrium constant, and the thermodynamic parameter calculated by $b = K$ or K_a is called the apparent thermodynamic parameter [27]. Eqs. (3)–(5) were defined as follows:

$$\Delta G = -RT \ln K \tag{3}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{4}$$

$$\Delta H = R\left(\frac{T_1 \cdot T_2}{T_2 \cdot T_1}\right) \cdot \ln\left(\frac{K_a, T_2}{K_a, T_1}\right) \tag{5}$$

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, 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 by step approximation method, and Origin 9.0 was adopted to improve data plotting. SPSS 16.0 statistical

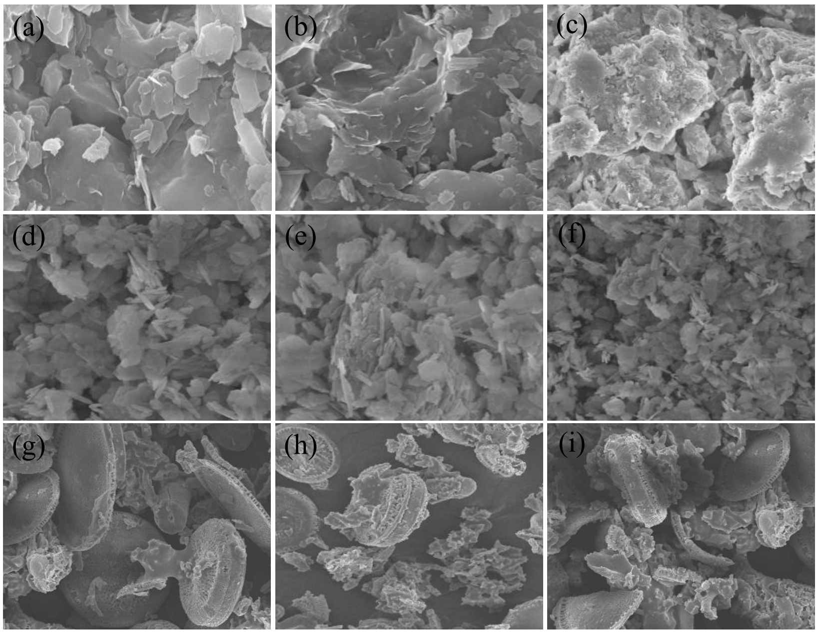

Fig. 1. SEM images of B (a), BS-B (b), Mg-BS-B (c), K (d), BS-K (e), Mg-BS-K (f), D (g), BS-D (h), and Mg-BS-D (i).

analysis software was used to process the experimental data for variance and correlation analysis.

3. Results and discussion

3.1. Basic physical and chemical characteristics of tested soil samples

The basic physical and chemical properties of each tested sample are shown in Table 1. When clay was modified by BS, the pH of BS-B decreased, and that of BS-K and BS-D increased. Compared with BS-clay, the pH of Mg-BS-clay changed slightly. Under the same modification conditions, the CEC and specific surface area (S_{BET}) of each sample changed as follows: original clay > Mg-BS-clay > Mg-BS-clay. The above results can be mainly attributed to the long carbon chain of BS that covers the exchangeable cations and surface pores on the clay surface, resulting in the reduction of the CEC and S_{BET} of BS-clay. The exchangeable ions and pores on the surface of Mg-BS-clay gradually increased with the loading of Mg, thereby increasing the CEC and S_{BET} again.

3.2. Morphology features of the tested samples

Fig. 1 shows the scanning electron microscopy (SEM) images of the different tested samples. The original B and K have layered structures and a large layer space. After modification by BS, the surface of BS-B and BS-K became smooth and layer space of BS-B and BS-K were covered. Compared with BS-B and BS-K, the surface of Mg-BS-B and Mg-BS-K became rough and evenly covered with particles. The surface of D contained many tubular holes, numerous particles were attached to the surface of BS-D and Mg-BS-D, and some of the pores were covered.

3.3. Isothermal adsorption characteristics of the tested materials

At 25°C, pH = 6, and ionic strength of 0.1 mol/L, the isothermal adsorption characteristics of TC, CTC, and OTC on the tested materials are shown in Fig. 2. With the increase of the equilibrium concentration, the adsorption capacity of each material for the antibiotics all increased and gradually tended to saturate, and presented the "L" type of adsorption isotherm. The adsorption isotherms of the antibiotics were fitted by using the Langmuir adsorption isotherm equation, and the resulting parameters are shown in Table 2. The fitting correlation coefficients reached a very significant level ($P < 0.01$), indicating that the adsorption processes of TC, CTC, and OTC on the tested samples can be described well by the Langmuir model. This result indicates that the adsorption of each sample for the three antibiotics is mainly monolayer adsorption [28].

The maximum adsorption amount (q_m) of antibiotics for the tested sample were 1.70–5.21 mol/kg (TC), 1.80–5.94 mol/kg (CTC), and 1.81–6.28 mol/kg (OTC), respectively, and the q_m values followed the order OTC > CTC > TC on the same sample. For the same antibiotic, the q_m values of the different samples followed the order Mg-BS-clay > BS-clay > Clay. Compared with the original clay, the q_m values of TC, CTC, and OTC on BS-clay increased by 23.80%–44.14%, 2.30%–71.90%, and 2.03%–41.34%, respectively. Under the same modification conditions, the q_m values of the different samples followed the order B > K > D. This result may be due to the large CEC and S_{BET} of bentonite (Table 1), which can lead to the high ion exchange with antibiotics [26]. The

Table 1
Physico-chemical properties of the tested samples

Tested sample	pH	Cation exchange capacity (mmol/kg)	Specific surface area (m²/g)
B	10.21	1,001.25	62.88
BS-B	8.22	552.23	7.34
Mg-BS-B	8.03	652.65	23.56
K	6.90	88.69	11.42
BS-K	7.12	58.23	7.45
Mg-BS-K	7.24	59.32	9.24
D	7.20	330.12	67.26
BS-D	7.44	162.58	6.37
Mg-BS-D	7.34	190.39	30.23

Table 2
Langmuir fitting parameters of the adsorption isotherms

Antibiotics	Composite material	Correlation coefficient (r)	q_m (mol/kg)	b
TC	B	0.9933**	2.31	30.95
	BS-B	0.9998**	4.99	31.28
	Mg-BS-B	0.9988**	5.21	67.70
	D	0.9967**	1.70	13.53
	BS-D	0.9973**	2.55	29.35
	Mg-BS-D	0.9989**	4.17	23.68
	K	0.9952**	2.01	21.89
	BS-K	0.9977**	3.82	29.92
	Mg-BS-K	0.9979**	4.62	58.40
CTC	B	0.9982**	2.77	24.68
	BS-B	0.9997**	5.69	63.62
	Mg-BS-B	0.9995**	5.94	116.81
	D	0.9991**	1.80	18.45
	BS-D	0.9993**	3.27	64.26
	Mg-BS-D	0.9978**	4.59	69.53
	K	0.9988**	2.13	28.00
	BS-K	0.9990**	4.81	40.75
	Mg-BS-K	0.9984**	5.49	58.42
OTC	B	0.9987**	3.87	30.33
	BS-B	0.9986**	5.94	124.46
	Mg-BS-B	0.9972**	6.28	143.72
	D	0.9966**	1.81	18.11
	BS-D	0.9997**	3.51	53.72
	Mg-BS-D	0.9977**	4.96	66.31
	K	0.9977**	2.38	29.65
	BS-K	0.9993**	5.17	47.75
	Mg-BS-K	0.9993**	6.11	64.91

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

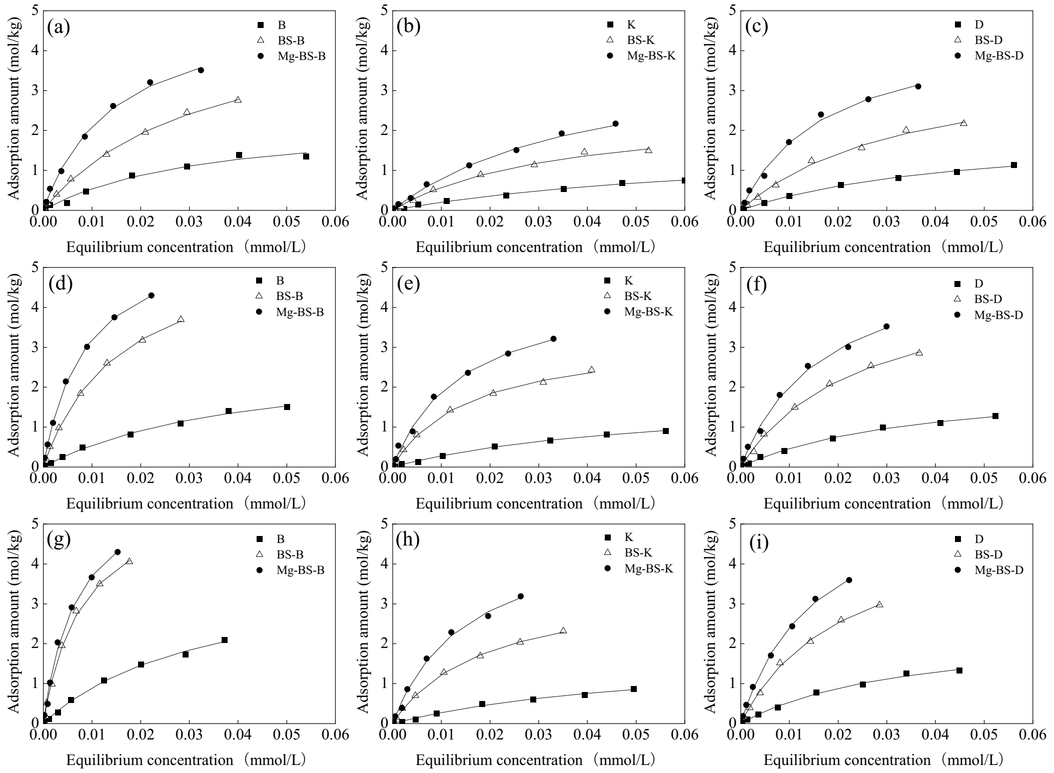

Fig. 2. Isothermal adsorption of TC (a–c), CTC (d–f), and OTC (g–i) on the test materials.

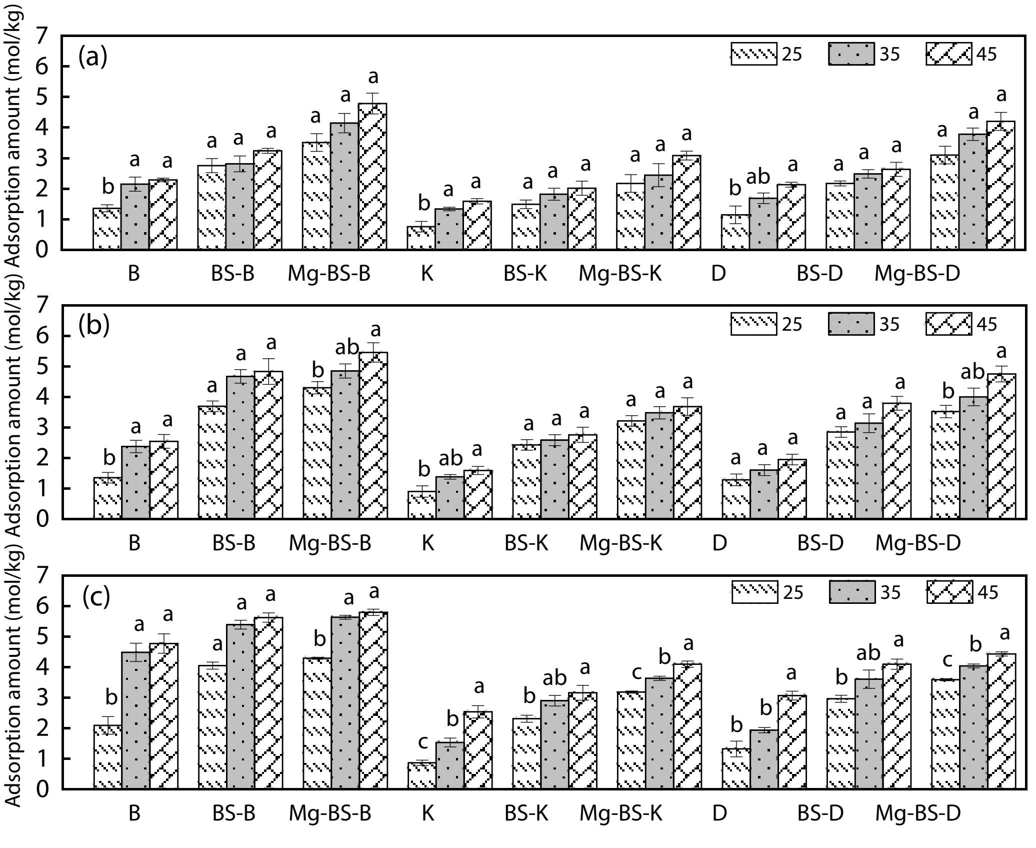

Fig. 3. Influence of temperature on the adsorption of TC (a), CTC (b), and OTC (c). *Note*: Different lowercase letters indicate significant differences among the treatments at the 0.05 level.

Table 3
Thermodynamic parameters of three antibiotics adsorption

Antibiotics	Composite material	25°C			45°C		
		ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol·K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol·K)
TC	B	–8.51	20.61	97.68	–10.46	20.61	97.68
	BS-B	–8.53	6.40	50.09	–9.54	6.40	50.09
	Mg-BS-B	–10.45	12.26	76.18	–11.97	12.26	76.18
	D	–6.46	29.36	120.12	–8.86	29.36	120.12
	BS-D	–8.38	11.87	67.89	–9.73	11.87	67.89
	Mg-BS-D	–7.84	13.83	72.69	–9.30	13.83	72.69
	K	–7.65	24.59	108.15	–9.81	24.59	108.15
	BS-K	–8.42	7.66	53.95	–9.50	7.66	53.95
	Mg-BS-K	–10.08	12.02	74.14	–11.56	12.02	74.14
CTC	B	–7.95	24.90	110.17	–10.15	24.90	110.17
	BS-B	–10.29	10.61	70.10	–11.70	10.61	70.10
	Mg-BS-B	–11.80	9.40	71.10	–13.22	9.40	71.10
	D	–7.23	22.20	98.69	–9.20	22.20	98.69
	BS-D	–10.32	4.98	51.32	–11.35	4.98	51.32
	Mg-BS-D	–10.51	5.36	53.23	–11.58	5.36	53.23
	K	–8.26	16.48	82.96	–9.92	16.48	82.96
	BS-K	–9.19	11.25	68.55	–10.56	11.25	68.55
	Mg-BS-K	–10.08	11.79	73.35	–11.55	11.79	73.35
OTC	B	–8.46	32.47	137.27	–11.20	32.47	137.27
	BS-B	–11.96	12.94	83.51	–13.63	12.94	83.51
	Mg-BS-B	–12.31	11.84	81.01	–13.93	11.84	81.01
	D	–7.18	42.11	165.30	–10.49	42.11	165.30
	BS-D	–9.88	12.32	74.45	–11.36	12.32	74.45
	Mg-BS-D	–10.40	9.92	68.14	–11.76	9.92	68.14
	K	–8.40	33.13	139.30	–11.19	33.13	139.30
	BS-K	–9.58	12.71	74.78	–11.08	12.71	74.78
	Mg-BS-K	–10.34	8.30	62.53	–11.59	8.30	62.53

affinity constant (*b*) of each tested sample for antibiotic adsorption was maintained in the range of 13.53–143.72, implying a strong adsorption affinity and the spontaneous adsorption reaction [29].

3.4. Influence of temperature on antibiotics adsorption

The adsorption amount of TC, CTC, and OTC on each tested sample varied with the temperature as shown in Fig. 3. In the range of 25°C–45°C, the adsorption amount of antibiotics increased with the increase of temperature, showing a positive temperature effect. The TC, CTC, and OTC increases on each tested sample were 17.62%–110.54%, 13.47%–88.04%, and 23.42%–190.90%, respectively. Compared with the original clay, the CTC adsorption amount of BS-clay increased the most, may be because the adsorption of antibiotics is mainly due to the ion exchange and complexation. These adsorption processes are all chemical reactions, and the increase of temperature intensifies the random thermal movement between molecules, which is conducive to the contact between the antibiotics and the adsorption sites on the surface of the tested materials [19–26].

The adsorption thermodynamic parameters of antibiotics can be seen in Table 3. At 25°C and 45°C, the antibiotics adsorption free energy (ΔG) on the tested materials were all negative, indicating that the adsorption of TC, CTC, and OTC was a spontaneous process. The case $|\Delta G_{45}| > |\Delta G_{25}|$ showed that the higher the temperature was, the stronger the adsorption reaction spontaneity would be. The results of the endothermic reaction are consistent with temperature effect. The enthalpy changes (ΔH) of antibiotics adsorption on all the tested samples were positive, indicating that the adsorption was endothermic reaction. The adsorption of antibiotics on each mixed soil sample showed an entropy increase reaction, and the entropy value (ΔS) was between 50.09 and 165.30. This phenomenon indicates that the adsorption process has a high degree of chaos and multiple adsorption mechanisms.

3.5. Influence of pH on adsorption of three antibiotics

Fig. 4 shows the influence of pH on the adsorption of the three antibiotics. In the pH range of 2 to 10, the adsorption amount of TC, CTC, and OTC of each tested sample increased first and then decreased and maintained the

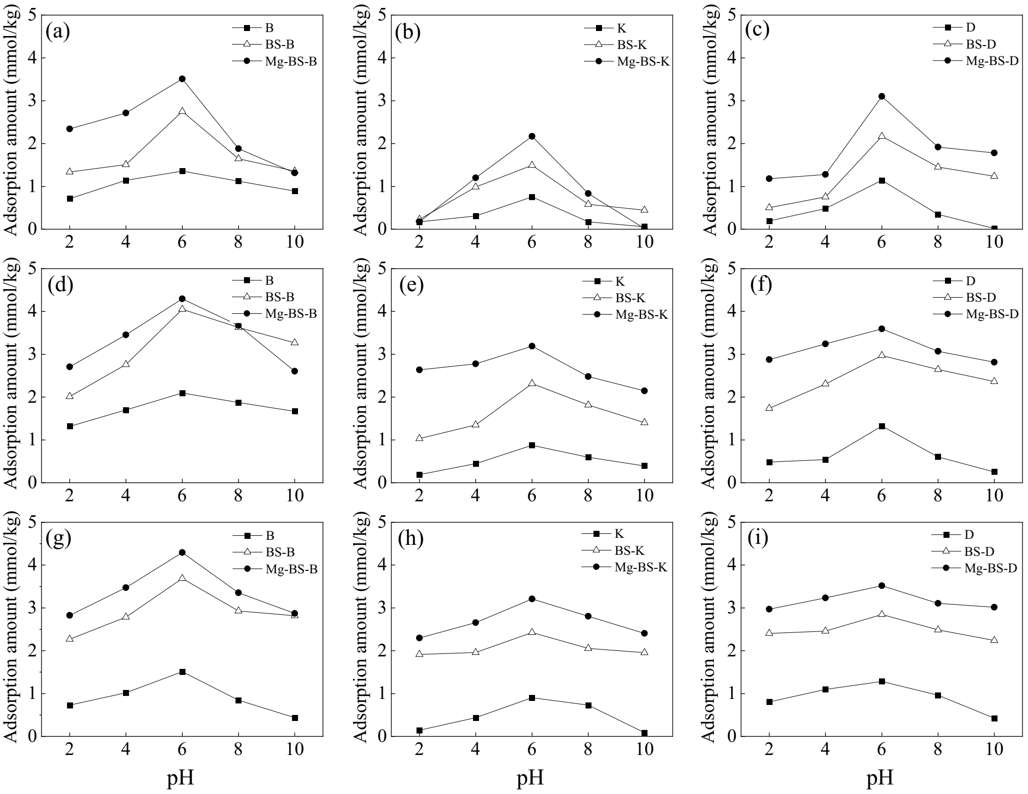

Fig. 4. Influence of pH on the adsorption of TC (a–c), CTC (d–f), and OTC (g–i).

maximum value at pH = 6. With the increase of pH in the range of 2–6, the increments of the TC, CTC, and OTC adsorption amounts were 1.58–2.00, 0.44–1.47, and 1.55–2.04 mol/kg, respectively. The pH of the solution greatly influenced the adsorption effect of the tested materials, which may be related to the existence of antibiotics in aqueous solution. Three ionizable groups were found in the molecular structures of the antibiotics, and ionization equilibrium constants pK_{a1}, pK_{a2}, and pK_{a3} were 3.30–3.57, 7.49–7.69, and 9.44–9.88, respectively. The antibiotics with pH < 3.30 are positively charged; that is, the pH between 3.30 and 7.69 is positively or negatively charged, and that with pH > 9.50 exists as an anion [17]. Therefore, under acidic conditions, antibiotics can be combined with the negative charge on the surface of the tested materials by cation exchange, thereby increasing the adsorption. With the increasing pH, the proportion of negative charge in the antibiotics molecule increases, and the adsorption decreases gradually [30].

3.6. Influence of ionic strength on adsorption of three antibiotics

Ionic strength is a key factor affecting the adsorption performance and an auxiliary means of studying the adsorption mechanism. Increasing the ionic strength can weaken the electrostatic interaction between the adsorbent and the adsorbate and enhance the hydrophobic effect [31]. Table 4 indicated that with the increase of the ionic strength from 0.01 to 0.5 mol/L, the adsorption amount of antibiotics on the test samples slightly decreased, and the decrease ranges were 15.17%–84.17% (TC), 16.07%–68.07% (CTC), and 16.30%–76.54% (OTC). This phenomenon may be due to the competitive adsorption of cations in the structure with the increase of the ionic strength, resulting in a decrease in the adsorption amount of all the tested soil samples for the three antibiotics. This result is consistent with that of Zhang et al. [30].

3.7. Performance comparison of other materials in antibiotics adsorption

Clay has a high specific surface area and abundant surface adsorption sites and can have a weak ion exchange effect on antibiotics. During the modification of clay with BS, BS was easily combined with the negative charge sites on the outer surface of the clay by the positive charge group $-N^+$ end. The antibiotics were adsorbed through negative charge points, such as the carboxyl group of BS-clay and the residual negative charge of clay through ion exchange. Moreover, antibiotics and the long carbon chain of BS-12 formed hydrophobic bonds on the surface of BS-clay, and thus the q_m values of the antibiotics in BS-clay were higher than those of clay [32]. After loading by Mg, the specific surface area and surface adsorption sites of BS-clay improved, and the antibiotics adsorption amount of Mg-BS-clay increased [33]. Compared with the above result, the amphoteric-clay-based composite material used in water improvement exhibited a high adsorption capacity for antibiotics and is thus a good improvement material. Table 5 shows the comparison of the adsorption amount of Mg-BS-clay with those of other adsorbents. The

Table 4
Effect of ionic strengths adsorption on different materials

Antibiotics	Soil sample	Adsorption amount (mol/kg)		
		0.01 mol/L	0.1 mol/L	0.5 mol/L
TC	B	1.78a ± 0.12	1.36ab ± 0.14	1.08b ± 0.07
	BS-B	3.64a ± 0.23	2.75b ± 0.08	1.03c ± 0.20
	Mg-BS-B	4.73a ± 0.07	3.51b ± 0.11	3.23b ± 0.24
	K	0.97a ± 0.12	0.75a ± 0.07	0.15b ± 0.12
	BS-K	2.19a ± 0.26	1.49ab ± 0.23	0.60b ± 0.14
	Mg-BS-K	3.14a ± 0.18	2.17b ± 0.10	1.06c ± 0.09
	D	1.28a ± 0.12	1.14a ± 0.14	1.08a ± 0.07
	BS-D	3.28a ± 0.23	2.17ab ± 0.28	1.08b ± 0.08
	Mg-BS-D	3.31a ± 0.12	3.10a ± 0.11	1.69b ± 0.24
CTC	B	2.33a ± 0.17	1.51b ± 0.20	1.40b ± 0.13
	BS-B	4.53a ± 0.17	3.69ab ± 0.20	3.40b ± 0.23
	Mg-BS-B	4.59a ± 0.20	4.30ab ± 0.26	3.50b ± 0.22
	K	1.86a ± 0.17	0.90b ± 0.08	0.59b ± 0.23
	BS-K	2.51a ± 0.17	2.43a ± 0.08	1.66b ± 0.13
	Mg-BS-K	3.56a ± 0.16	3.21a ± 0.21	2.99a ± 0.09
	D	1.81a ± 0.17	1.28ab ± 0.25	0.87b ± 0.08
	BS-D	3.54a ± 0.18	2.85a ± 0.23	1.90b ± 0.08
	Mg-BS-D	3.61a ± 0.22	3.52b ± 0.23	2.11b ± 0.16
OTC	B	3.66a ± 0.12	2.10b ± 0.15	1.65b ± 0.13
	BS-B	4.69a ± 0.12	4.05b ± 0.17	3.83b ± 0.07
	Mg-BS-B	4.97a ± 0.17	4.29ab ± 0.20	4.16b ± 0.13
	K	1.73a ± 0.18	0.87b ± 0.12	0.41b ± 0.07
	BS-K	3.34a ± 0.12	2.32b ± 0.24	1.60b ± 0.13
	Mg-BS-K	3.42a ± 0.20	3.19ab ± 0.23	2.42b ± 0.08
	D	1.68a ± 0.12	1.33ab ± 0.14	0.95b ± 0.01
	BS-D	3.75a ± 0.11	2.97ab ± 0.36	2.35b ± 0.14
	Mg-BS-D	4.44a ± 0.16	3.59b ± 0.21	2.61c ± 0.08

Note: Different lowercase letters indicate significant differences among the temperature treatments at the 0.05 level.

comparison shows that the materials used in this paper have a good adsorption effect on antibiotics. The adsorption amount of the material used, which is a kind of antibiotic adsorption material with good performance, is several times higher than of those of the other materials.

Correlation analysis was conducted on the adsorption amount and properties of each tested sample for antibiotics, and the correlation coefficient changed from 0.0270 to 0.4064. Nearly no correlation existed between pH, CEC of the samples and the adsorption amount of antibiotics. S_{BET} was negatively correlated with the adsorption amount of antibiotics. These results indicate that the adsorption of antibiotics is unrelated to the physico-chemical properties of the material itself but mainly depends on the properties and charge changes of the antibiotics.

4. Conclusion

The q_m values of the antibiotics were 1.70–5.21 mol/kg (TC), 1.80–5.94 mol/kg (CTC), and 1.81–6.28 mol/kg (OTC). Under the same modification conditions, the q_m values of the antibiotics followed the order Mg-BS-B > Mg-BS-K > Mg-BS-D. Increasing the temperature was conducive to the adsorption of the three antibiotics by each sample. The thermodynamic parameters showed that the TC, CTC, and OTC adsorption was spontaneous, endothermic and entropic-increasing processes. The adsorption amount of TC, CTC, and OTC on each soil sample increased first and then decreased and reached the peak value at pH = 6. The adsorption amounts of the three antibiotics decreased with the increase of the ionic strength. For practical application, the proposed BS modification has economic, ecological, and effective advantages and high application value for water pollution remediation. This work will provides a reference for the utilization of clay resources and the remediation of antibiotic-contaminated water.

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Table 5
Comparison of the adsorption amount of Mg-BS-clay with other adsorbents

Antibiotics	Adsorbent	Adsorption conditions	Maximum adsorption capacities (mol/kg)	References
TC	Montmorillonite	pH 7 and 25°C	1.06	Parolo et al. [34]
	Magnetic biochar	pH 7 and 20°C	0.50	Deng et al. [29]
	Mg-BS-B	pH 6 and 25°C	5.21	This study
CTC	Manganese ferrite-loaded swine manure hydrochar	pH 7 and 25°C	1.57	Minale et al. [35]
	Fe-loaded amphotropic bentonite	pH 3 and 40°C	3.39	Liu et al. [25]
	Mg-BS-B	pH 6 and 25°C	5.94	This study
OTC	Nano-hydroxyapatite	pH 8 and 25°C	0.66	Maria and Ciobanu et al. [36]
	CuMnAl-hydroxide	pH 7 and 50°C	0.54	Eniola et al. [37]
	Mg-BS-B	pH 6 and 25°C	6.28	This study

Conflict of interests

The authors declare that they have no conflict of interest.

References

[1] X.Y. Chen, Y. Liu, X. Fang, Z. Li, H.H. Pu, J.B. Chang, J.H. Chen, S. Mao, Ultratrace antibiotic sensing using aptamer/graphene-based field-effect transistors, Biosens. Bioelectron., 126 (2018) 664–671.

[2] J. Wang, X. Liu, Y. Dai, J. Ren, C. Peng, Effects of co-loading of polyethylene microplastics and ciprofloxacin on the antibiotic degradation efficiency and microbial community structure in soil, Sci. Total Environ., 741 (2020) 140463–140474.

[3] Y. Chen, R. Yin, L. Zeng, W. Guo, M. Zhu, Insight into the effects of hydroxyl groups on the rates and pathways of tetracycline antibiotics degradation in the carbon black activated peroxydisulfate oxidation process, J. Hazard. Mater., 14 (2021) 125256–125266.

[4] D. Hao, Y.X. Song, Y. Zhang, H.T. Fan, Nanocomposites of reduced graphene oxide with pure monoclinic-ZrO_2 and pure tetragonal-ZrO_2 for selective adsorptive removal of oxytetracycline, Appl. Surf. Sci., 543 (2021) 148810–148821.

[5] N. You, S. Chen, Y. Wang, H.T. Fan, L.N. Sun, T. Sun, In situ sampling of tetracycline antibiotics in culture wastewater using diffusive gradients in thin films equipped with graphene nanoplatelets, Environ. Res., 191 (2021) 110089–110099.

[6] F. Ma, Y. Gui, P. Liu, Y. Xue, W. Song, Functional fibrous materials-based adsorbents for uranium adsorption and environmental remediation, Chem. Eng. J., 390 (2020) 124597–124610.

[7] M.R. Abukhadra, A.M. El-Sherbeeny, M.A. El-Meligy, M. Luqman, Insight into carbohydrate polymers (chitosan and 2-hydroxyethyl methacrylate/methyl methacrylate) intercalated bentonite-based nanocomposites as multifunctional and environmental adsorbents for methyl parathion pesticide, Int. J. Biol. Macromol., 167 (2021) 335–344.

[8] A. Asdagh, I.K. Sani, S. Pirsa, S. Amiri, N. Shariatifar, H. Eghbaljoo-Gharehgheshlaghi, Z. Shabahang, A. Taniyan, Production and characterization of nanocomposite film based on whey protein isolated/copper oxide nanoparticles containing coconut essential oil and paprika extract, J. Polym. Environ., 29 (2021) 335–349.

[9] M.H. Moghaddam, R. Nabizadeh, M.H. Dehghani, B. Akbarpour, M. Yousefi, Performance investigation of zeolitic imidazolate framework-8 (ZIF-8) in the removal of trichloroethylene from aqueous solutions, Microchem. J., 150 (2019) 104185–104196.

[10] C. Wu, X. Lou, A. Huang, M. Zhang, L. Ma, Thermodynamics and kinetics of pretilachlor adsorption: implication to controlled release from organobentonites, Appl. Surf. Sci., 190 (2020) 105566–107778.

[11] A.E. Angkawijaya, S.P. Santoso, V. Bundjaja, F.E. Soetaredjo, S. Ismadji, Studies on the performance of bentonite and its composite as phosphate adsorbent and phosphate supplementation for plant, J. Hazard. Mater., 399 (2020) 123130, doi: 10.1016/j.jhazmat.2020.123130.

[12] Y.E. Maataoui, M.E. M'rabet, A. Maaroufi, A. Dahchour, Spiramycin adsorption behavior on activated bentonite, activated carbon and natural phosphate in aqueous solution, Environ. Sci. Pollut. Res., 26 (2019) 15953–15972.

[13] C. Science, A.M. Saddam, Adsorption of tetracycline antibiotic from aqueous solutions using natural Iraqi bentonite, Egypt. J. Chem., 64 (2021) 5511–5519.

[14] C. Oliveira, A.L.M.D. Oliveira, L. Chantelle, R. Landers, M.G. Fonseca, Zinc(II) modified hydroxyapatites for tetracycline removal: Zn(II) doping or ZnO deposition and their influence in the adsorption, Polyhedron, 194 (2020) 114879, doi: 10.1016/j.poly.2020.114879.

[15] R. Gao, D. Liu, Y. Huang, G. Li, Preparation of diatomite-modified wood ceramics and the adsorption kinetics of tetracycline, Ceram. Int., 46 (2020) 19799–19806.

[16] P. Yao, S.B. Li, Y. Liu, Q.M. Zhang, C.L. Ji, H.L. Nie, Preparation and characterization of HTMAC/KH550/bentonite adsorbents for methyl orange wastewater, Chem. Ind. Prog., 4 (2017) 1374–1380.

[17] M.X. Wang, H.Y. Deng, W.B. Li, J.M. Ouyang, Z.S. Lu, Z.Q. Zhang, Tetracycline adsorption by clay under the coexistence of three extracts from an invasive plant, Desal. Water Treat., 237 (2022) 237–246.

[18] Z. Wang, Y. Muhammad, R. Tang, C. Lu, H. Zhang, Dually organic modified bentonite with enhanced adsorption and desorption of tetracycline and ciprofloxacine, Sep. Purif. Technol., 274 (2021) 119059–119071.

[19] X.X. Wang, Z.F. Meng, X. Liu, T. Wang, X.L. Hu, X.X. Sun, Adsorption of tetracycline and norfloxacin by BS-18 amphteric modified bentonite, Environ. Sci., 42 (2021) 2334–2342.

[20] E.C. Gillispie, S.E. Taylor, N.P. Qafoku, M.F. Hochella, Impact of iron and manganese nano-metal-oxides on contaminant interaction and fortification potential in agricultural systems–a review, Environ. Chem., 16 (2019) 333–347.

[21] A. Stockdale, W. Davison, Z. Hao, J. Hamilton-Taylor, The association of cobalt with iron and manganese (oxyhydr) oxides in marine sediment, Aquat. Geochem., 16 (2010) 575–585.

[22] H. Xi, H. Jiang, D. Zhao, A.H. Zhang, J. Zhang, Highly selective adsorption of phosphate from high-salinity water environment

using MgO-loaded and sodium alginate-immobilized bentonite beads, J. Cleaner Prod., 33 (2021) 127773–127786.

[23] A.P. Fagundes, A.F.V.D. Silva, B.B.D. Morais, D.L.P. Macuvele, C. Soares, A novel application of bentonite modified with copper ions in the tetracycline adsorption: an experimental design study, Mater. Lett., 291 (2021) 129552–129555.

[24] S.B. Bu, Z.F. Meng, S. Yek, M.F. Zhang, T. Wang, S. Ren, L.K. Zhang, Adsorption and interaction of Cu^{2+} and Pb^{2+} on BS-12 amphoteric modified bentonites, Environ. Sci., 40 (2019) 4611–4619.

[25] Z.F. Liu, X. Fang, L.Y. Chen, B. Tang, F.M. Song, W.B. Li, Effect of acid–base modified biochar on chlortetracycline adsorption by purple soil, Sustainability, 240 (2022) 237–246.

[26] H.Y. Deng, X.W. Cao, W.B. Li, H, Zhang, H.X. He, D. Wang, L.P. Ren, Z.F. Meng, Effect of three additives on tetracycline adsorption by purple soil, Environ. Monit. Manage. Technol., 32 (2020) 68–71.

[27] L.Y. Chen, H.X. He, Y.L. Zhao, H.Q. He, S.L. Chen, W.B. Li, H.Y. Deng, Z.G. Ren, Influence of non-dissolved organic matter on the adsorption and aging of copper in riverbank soil, J. Agro-Environ. Sci., 40 (2021) 1696–1706.

[28] T. Wang, H.Y. Lu, M.F. Zhang, S.B. Bu, S. Ren, Effect of N-F doping ratio on terramycin adsorption performance of TiO_2/bentonite composites, J. Agro-Environ. Sci., 38 (2019) 2764–2771.

[29] H.Y. Deng, H.X. He, W.B. Li, T. Abbas, Z.F. Liu, Characterization of amphoteric bentonite-loaded magnetic biochar and its adsorption properties for Cu^{2+} and tetracycline, PeerJ, 10 (2022) e13030, doi: 10.7717/peerj.13030.

[30] Q. Zhang, G.Y. Huang, L. Zhao, Y.H. Dong, Influence of pH and ions on sorption of norfloxacin on humic acid, Chin. Environ. Sci., 31 (2011) 78–83.

[31] Y. Liu, K. Zhang, S. Xu, M. Yan, P.K.S. Lam, Heavy metals in the "plastisphere" of marine microplastics: adsorption mechanisms and composite risk, Gondwana Res., 4 (2021) 327–339.

[32] Y. Zou, H.Y. Deng, M. Li, Y.H. Zhao, W.B. Li, Enhancing tetracycline adsorption by riverbank soils by application of biochar-based composite materials, Desal. Water Treat., 207 (2020) 332–340.

[33] W.B. Li, X.Y. Chen, H.Y. Deng, D. Wang, J.C. Jiang, Y.Z. Zeng, L Kang, Z.F. Meng, Effects of exogenous biochar on tetracycline adsorption by different riverbank soils from Sichuan and Chongqing section of Jialing River, Chin. J. Soil Sci., 51 (2020): 46–54.

[34] M.E. Parolo, M.C. Savini, J.M. Vallés, M.T. Baschini, M.J. Avena, Tetracycline adsorption on montmorillonite: pH and ionic strength effects, Appl. Clay Sci., 40 (2008) 179–186.

[35] M. Minale, A. Guadie, Y. Liu, Y. Meng, J. Zhao, Insight into adsorption behavior of chlortetracycline and cadmium in aqueous solution using a novel manganese ferrite loaded swine manure hydrochar, J. Environ. Chem. Eng., 9 (2021) 106785, doi: 10.1016/j.jece.2021.106785.

[36] H. Maria, G. Ciobanu, Studies on adsorption of oxytetracycline from aqueous solutions onto hydroxyapatite, Sci. Total Environ., 628/629 (2018) 36–43.

[37] J.O. Eniola, R. Kumar, A.A. Al-Rashdi, M.A. Barakat, Hydrothermal synthesis of structurally variable binary CuAl, MnAl and ternary CuMnAl hydroxides for oxytetracycline antibiotic adsorption, J. Environ. Chem. Eng., 8 (2020) 103535, doi: 10.1016/j.jece.2019.103535.