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Adsorption of Cu^{2+} and Cd^{2+} on sierozem compositely modified by zwitterionic and anionic modifier

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ABSTRACT

This study aimed to investigate the adsorption of heavy metal ions onto zwitterionic and anionic modified sierozem, dodecyl dimethyl betaine (zwitterionic modifier, BS) and sodium dodecyl sulfate (anionic modifier, SDS), which were used to simultaneously modify sierozems. The adsorption characteristics of Cu^{2+} and Cd^{2+} on each composite modified sierozem were studied by batch method, and the effect of temperature, pH, and ionic strength on adsorption were compared. The following results were obtained: (1) the adsorption isotherms of Cu^{2+} and Cd^{2+} in different modified sierozems followed the Langmuir model. The adsorption capacities of Cu^{2+} and Cd^{2+} were in the order of BS+SDS-modified > BS-modified > unmodified sierozem. With the increase of modified proportion of SDS, the amount of Cu^{2+} and Cd^{2+} adsorbed onto BS+SDS-modified sierozem increased. Cu^{2+} has a higher adsorption amount on the same modified sierozem than Cd^{2+}. (2) The increase of temperature inhibited Cu^{2+} and Cd^{2+} adsorption in BS+SDS modified sierozems but promoted Cu^{2+} and Cd^{2+} adsorption in BS-modified and unmodified sierozems. Low ionic strength and high pH promoted the Cu^{2+} and Cd^{2+} adsorption in all tested modified sierozems. (3) The adsorption of Cu^{2+} and Cd^{2+} onto different sierozem samples showed a spontaneous, entropy-increasing, and endothermic process on CK and BS-modified sierozem and spontaneous, entropy-increasing, and exothermic process on BS+SDS-modified sierozem. The spontaneity and entropy of Cu^{2+} adsorption were higher than those of Cd^{2+}.

Keywords: Sierozem; Dodecyl dimethyl betaine; Sodium dodecyl sulfate; Heavy metal; Adsorption mechanism

1. Introduction

Environmental problems are becoming increasingly serious with the development of the economy. Contaminants containing heavy metals that enter the soil have significantly deteriorated the soil environment [1–3]. Accordingly, the use of effective methods to control and reduce soil heavy metal pollution has become a focus in current research [4–6]. Organic substance can fix pollutants and reduce pollutants migration in soil, and then avoid being absorbed by the plant [7,8]. Therefore, organic modifiers are usually used to modify clay minerals or soil to improve the adsorption capacity of heavy metal pollution, and these materials are important for the protection of the soil environment, groundwater resources, and human health [9,10].

Modification by surfactants can enhance the adsorption capacity of heavy metal by soil or clay [11–14]. The adsorption capacity of Cd^{2+} on dodecyl dimethyl betaine (BS-12) modified bentonite and yellow-brown soil has been enhanced by 1.01–1.08 and 1.57–1.64 times than that

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on raw samples, respectively [15,16]. The amount of Cd^{2+} adsorbed onto modified bentonite and yellow-brown soil decreased with the increase of ionic strength. Cu^{2+} adsorption of clay has been enhanced by modified with BS-12 with a value that is 1.03–1.56 times higher than that of unmodified ones [17], and the temperature effect changed when modified with different modifier [18]. After the modification by zwitterionic surfactants, the adsorption capacity of Cu^{2+} on bentonite increased with the increase of temperature and pH but decreased with the increase of ionic strength. Upon modification with zwitterionic surfactants, the adsorption capacity of Cu^{2+} on purple soil decreased with the increase of temperature and ionic strength but increased with the increase of pH [19]. The adsorption mechanisms of heavy metal ions on zwitterionic modified clay or soil mainly involve ion exchange, electrostatic attraction, and complexation [20]. The adsorption of heavy metals by zwitterionic surfactants modified substrates has been widely reported. The substrates mainly include pure clay minerals or the soil in southwest China.

Sierozem in northwest China was simultaneously modified by zwitterionic and anionic modifier, and the adsorption effect of Cu^{2+} and Cd^{2+} was studied. The amount of pollutants adsorbed is expected to be greatly increased, and limited studies have been conducted in this field. This paper studied the adsorption characteristics of Cu^{2+} and Cd^{2+} in sierozem modified by BS-12 and sodium dodecyl sulfate (SDS), and the effect of various temperatures, pH values, and ionic strength on adsorption. This study provides a theoretical and practical basis for the remediation of heavy metal pollution in the environment by compositely modified soil.

2. Materials and methods

2.1. Experimental materials

Dodecyl dimethyl betaine was used as zwitterionic modifier and referred to as BS-12 (BS, analytic reagent, Tianjin Xingguang Auxiliary Factory, China). SDS (analytic reagent, Tianjin Dingshengxin Chemical Co., Ltd., China) was used as anionic modifier. The structural formulas of BS-12 and SDS are shown in Fig. 1.

The tested sample (sierozem) was collected from farmland in Anningqu Town of Urumqi City, and the surface (0–25 cm) samples were collected using the S-point method in a typical area. Sierozem was air-dried and ground, sieved through a 100-mesh nylon sieve, and prepared for use. The pH of sierozem was 8.85, the cation exchange capacity (CEC) was 305.16 mmol/kg, and total organic carbon was 11.91 g/kg.

Solutions of heavy metal pollutants Cu^{2+} and Cd^{2+} were prepared using $CuSO_4{\cdot}5H_2O$ (analytic reagent, Anhui Yuxuan Technology Co., Ltd., China) and $CdSO_4{\cdot}8H_2O$ (analytic reagent, Fuchen Chemical Reagent Factory, China), respectively.

2.2. Preparation of compositely modified sierozem

A wet method was used to prepare compositely modified sierozem [21]. In this method, a certain weight of sierozem was prepared for modification, slowly added to the prepared BS-12 solution with a sierozem/water ratio of 1:10, and then dispersed by ultrasound at 60°C for 3 h. The samples were centrifuged at 4,800 rpm for 20 min, and the supernatant was separated. BS-12-modified sierozem (zwitterionic-sierozem) could be obtained after washing thrice with deionized water. Zwitterionic-sierozem was dried at 60°C for 12 h and then passed through a 0.25 mm sieve. The compositely modification method was the same as the zwitterionic modification, in which zwitterionic-sierozem was prepared for modification, and then SDS was used to modify the zwitterionic-sierozem to obtain the compositely modified sierozem. The dosage of BS-12 and SDS were calculated using Eq. (1).

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

where W (g) is the quality of modifier. m (g) represents the mass of sierozem. CEC (mmol/kg) denotes the CEC of sierozem. M (g/mol) refers to the molecular mass of the modifier. R is the modified proportion. b stands for the content of the modifier product (mass fraction).

2.3. Experimental design

2.3.1. Tested compositely modified sierozem

BS modification was set at three proportions of 50%, 100%, and 150% by the CEC of sierozem, expressed as 50BS, 100BS, and 150BS, respectively. SDS was then modified on the basis of BS modification, and the composite modification ratios were set at 50BS+50SDS, 50BS+100SDS, 50BS+150SDS, 100BS+50SDS, 100BS+100SDS, 100BS+150SDS, 150BS+50SDS, 150BS+100SDS, and 150BS+150SDS. Unmodified sierozem was used as control (CK).

2.3.2. Concentration gradient of Cu^{2+} and Cd^{2+}

The experiments were carried out by using the adsorption isotherm method. In the following experimental design,

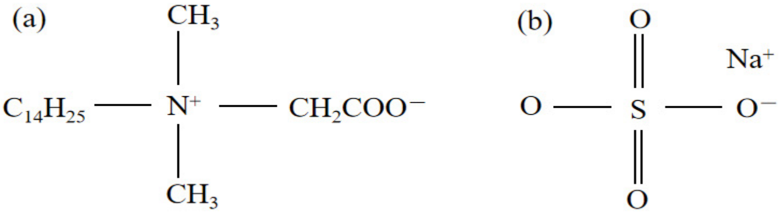

Fig. 1. Structural formulas of BS-12 (a) and SDS (b).

both Cu^{2+} and Cd^{2+} were set to nine concentration gradients of 5, 10, 20, 50, 100, 200, 300, 400, and 500 mg/L. The experimental temperature was set to 30°C, the pH was set to 7, and the ionic strength was 0.1 mol/L KNO_3. Three replicates were set for each treatment.

2.3.3. Environmental factors

The main environmental conditions were temperature, pH, and ionic strength. Three single-factor experiments were set considering the same environmental conditions.

The temperatures were set at 20°C, 30°C and 40°C regarding the actual temperature conditions of the local soil environment (pH value of the initial solution: 4; ionic strength: 0.1 mol/L KNO_3). The pH value of the contaminant solution was set to 3, 5, and 7 (the experimental temperature: 30°C; ionic strength: 0.1 mol/L KNO_3). The ionic strength was set to 0.05, 0.10, and 0.50 mol/L KNO_3 (pH value of the initial solution: 4; the experimental temperature: 30°C).

2.4. Experimental method

Equilibrium adsorption experiments were carried out by the batch method.

Approximately 0.5000 g of sample was weighed in nine 50 mL plastic centrifuge tubes, and 20.00 mL of Cu^{2+} (or Cd^{2+}) solution of the above series concentrations was added. At 30°C and 150 rpm, constant-temperature oscillation was carried out for 24 h (the preliminary kinetic experiments showed that adsorption equilibrium was reached after 24 h). The equilibrium adsorption of Cu^{2+} (or Cd^{2+}) in the supernatant was determined by centrifugation at 4,800 rpm for 20 min, the equilibrium adsorption amount of Cu^{2+} (or Cd^{2+}) was determined, and the equilibrium adsorption amounts of Cu^{2+} and Cd^{2+} were determined via subtraction.

Cu^{2+} and Cd^{2+} were determined by HITACHI Z-5000 atomic absorption spectrophotometer, the testing method was flame method, and the Zeeman effect was used to correct the background absorption. The above measurements were inserted into standard solutions for analytical quality control.

2.5. Data processing

2.5.1. Equilibrium adsorption amount

The equilibrium adsorption amount was calculated using Eq. (2):

$$q = \frac{V \times \left(C_0 - C_1\right)}{W_0} \tag{2}$$

where C_0 (mmol/L) and C_1 (mmol/L) are the initial and equilibrium concentrations of Cu^{2+} (or Cd^{2+}) in the solution, respectively. V (mL) is the volume of Cu^{2+} (or Cd^{2+}) solution added. W_0 (g) is the weight of the tested soil sample. q (mmol/kg) is the equilibrium adsorption amount of Cu^{2+} (or Cd^{2+}) on the tested soil.

2.5.2. Fitting of adsorption isotherms

The Langmuir isotherm was selected on the basis of the adsorption isotherm trend and the isothermal equation [Eq. (3)] is as follows [15]:

$$q = \frac{q_m b C_1}{1 + b C_1} \tag{3}$$

where q_m indicates the maximum adsorption amount of Cu^{2+} (or Cd^{2+}) on the different materials, mmol/kg; b represents the apparent equilibrium constant of the Cu^{2+} (or Cd^{2+}) adsorption, which can be used to measure the affinity of adsorption.

2.5.3. 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 is called the apparent thermodynamic parameters; Eqs. (4)–(6) are as follows [17]:

$$\Delta G = -RT \ln K \tag{4}$$

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

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

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, and SigmaPlot 10.0 software was adopted to improve data plotting.

3. Results and discussion

3.1. Cu^{2+} and Cd^{2+} adsorption on different modified sierozems

The adsorption isotherms of Cd^{2+} and Cu^{2+} on each test soil sample are shown in Fig. 2. Langmuir model was used to fit the adsorption isotherms of Cd^{2+} and Cu^{2+} on each modified sierozem (Table 1). The correlation coefficients all reached significant level ($P < 0.01$), indicating that the adsorption process of Cd^{2+} and Cu^{2+} on the modified sierozems was suitable for the Langmuir isothermal adsorption model. The equilibrium adsorption capacities of Cd^{2+} and Cu^{2+} on each modified sierozem were in the order of BS+150SDS > BS+100SDS > BS+50SDS > BS > CK.

The maximum adsorption amount (q_m) of Cu^{2+} on 50BS- and 100BS-modified sierozems were 1.26 and 1.33 times higher than those of CK, respectively. When SDS was secondly modified on BS-modified sierozems, the q_m values of Cu^{2+} on BS+SDS-modified sierozems were 1.01–1.18 and 1.09–1.46 times higher than those of BS-modified sierozems. Meanwhile, the q_m of Cu^{2+} on BS+SDS-modified sierozem was improved by 1.29–1.93 times compared with CK. The order of q_m of Cu^{2+} on each modified sierozem showed the same order as the equilibrium adsorption capacity in Fig. 2. Therefore, BS modification could improve and

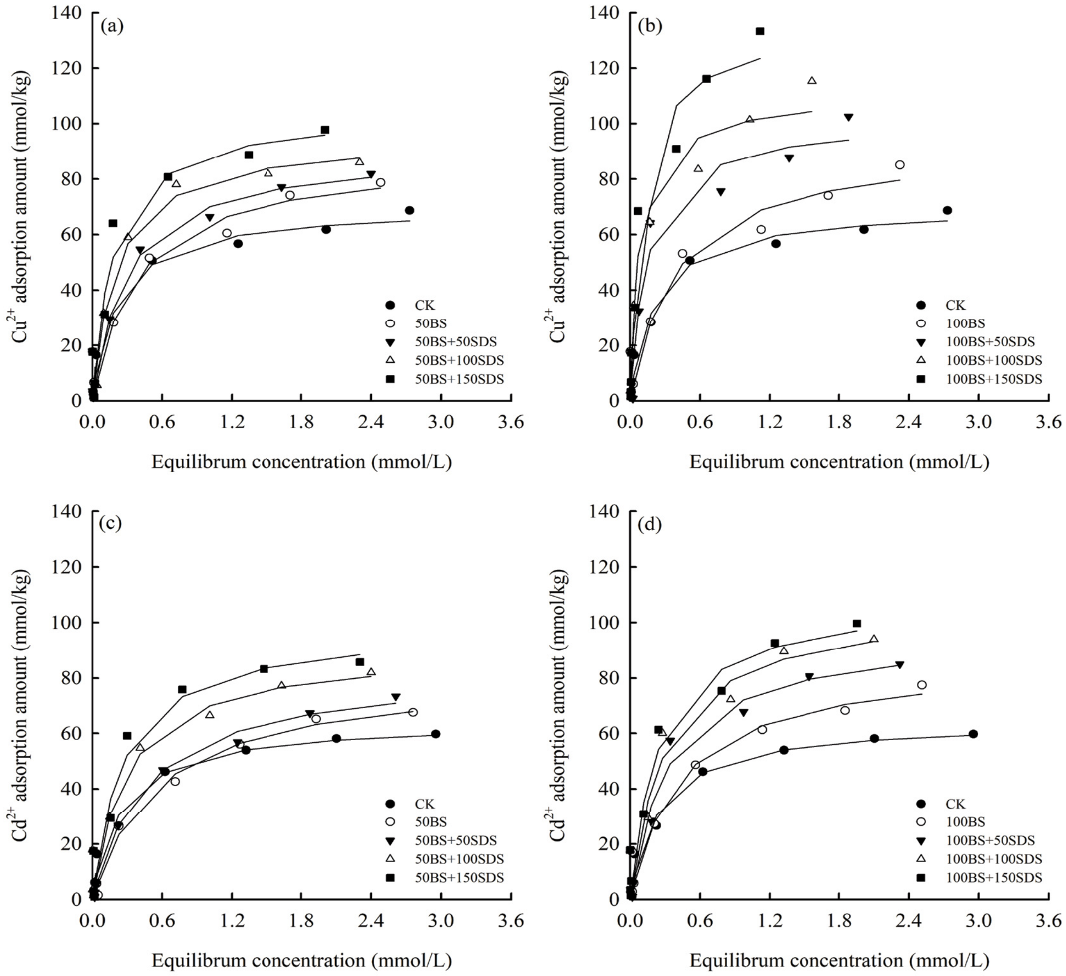

Fig. 2. Adsorption isotherms of Cu^{2+} and Cd^{2+} on different modified sierozems.

Table 1
Fitting parameters of Cu^{2+} and Cd^{2+} adsorption isotherms on different modified sierozems

Treatments	Cu^{2+}			Cd^{2+}		
	r	q_m	b	r	q_m	b
CK	0.9916**	70.06	459.80	0.9915**	64.54	404.52
50BS	0.9765**	88.45	261.01	0.9739**	82.00	396.45
50BS+50SDS	0.9800**	90.47	338.19	0.9849**	83.94	373.21
50BS+100SDS	0.9812**	95.55	476.60	0.9800**	90.47	338.19
50BS+150SDS	0.9782**	104.50	553.00	0.9823**	98.67	330.70
100BS	0.9755**	93.10	253.50	0.9857**	87.32	299.39
100BS+50SDS	0.9776**	101.49	669.74	0.9768**	96.84	227.74
100BS+100SDS	0.9814**	111.05	997.02	0.9779**	106.65	209.83
100BS+150SDS	0.9826**	135.50	925.96	0.9814**	109.27	175.13

Note: ** indicates significance at the $p = 0.01$ level ($r = 0.765$ at $p = 0.01$ when the degrees of freedom $f = 8$).

BS+SDS modification could observably promote the adsorption capacity of sierozem for Cu^{2+}. Moreover, q_m of BS+SDS-modified sierozem has a positive relationship with the proportion of SDS on BS-modified sierozem.

The q_m of Cd^{2+} on each modified sierozem ranged from 82.00 to 102.97 mmol/kg and had the same order as the equilibrium adsorption capacity in Fig. 2. In comparison with CK, the q_m of Cd^{2+} on 50BS- and 100BS-modified sierozem increased by 1.27 and 1.35 times, respectively. The q_m of Cd^{2+} on 50BS+50SDS-, 50BS+100SDS-, and 50BS+150SDS-modified sierozems were 1.02, 1.10, and 1.20 times higher than those on 50BS-modified sierozem, respectively. The q_m of Cd^{2+} on 100BS+SDS-modified sierozem was 1.11–1.25 times higher than that on 100BS-modified sierozem. The results indicate that BS modification improved the adsorption capacity of Cd^{2+} on sierozem, and increasing the BS modification proportion improved the adsorption capacity of Cd^{2+} onto BS-modified sierozem. Moreover, after being modified with SDS, the adsorption capacity of Cd^{2+} on BS-modified sierozem was remarkably enhanced. This result was similar to the Cu^{2+} adsorption in previous section.

The adsorption capacities of Cu^{2+} and Cd^{2+} on BS- and BS+SDS-modified sierozems were higher than those on CK, and had the trends of 100BS > 50BS > CK and BS+150SDS > BS+100SDS > BS+50SDS > CK. The q_m of Cu^{2+} on CK was 1.09 times higher than that of Cd^{2+}. The q_m of Cu^{2+} on 50BS- and 100BS-modified sierozems were 1.08 and 1.07 times higher than those of Cd^{2+}. The q_m of Cu^{2+} on BS+SDS-modified sierozems were 1.04–1.24 times higher than those of Cd^{2+}. The results showed that the adsorption capacity of Cu^{2+} on the tested samples was stronger than that of Cd^{2+}. The above finding was consistent with previous studies on Cd^{2+} adsorption onto BS+SDS-modified bentonite [20] and yellow-brown soil [16]. After being modified by BS, the q_m values of Cd^{2+} by bentonite were 1.36–1.39 and 3.63–5.44 times higher than those of sierozem and yellow-brown soil, respectively. Under the modification of BS+SDS, the q_m values of Cd^{2+} by bentonite were 1.75–3.45 and 4.85–6.41 times higher than those of sierozem and yellow-brown soil, respectively. The results indicated that the adsorption capacity of Cd^{2+} on modified clay was stronger than that of modified sierozem and yellow-brown soil with the trend of modified bentonite > modified sierozem > modified yellow-brown soil. This finding was obtained mainly because the CEC of bentonite (1,003.32 mmol/kg) was higher than that of sierozem (305.16 mmol/kg) and yellow-brown soil (184.7 mmol/kg).

3.2. Effect of temperature on Cu^{2+} and Cd^{2+} adsorption

Fig. 3 shows the adsorption changes of Cd^{2+} and Cu^{2+} on each tested sample at 20°C–40°C. When the temperature

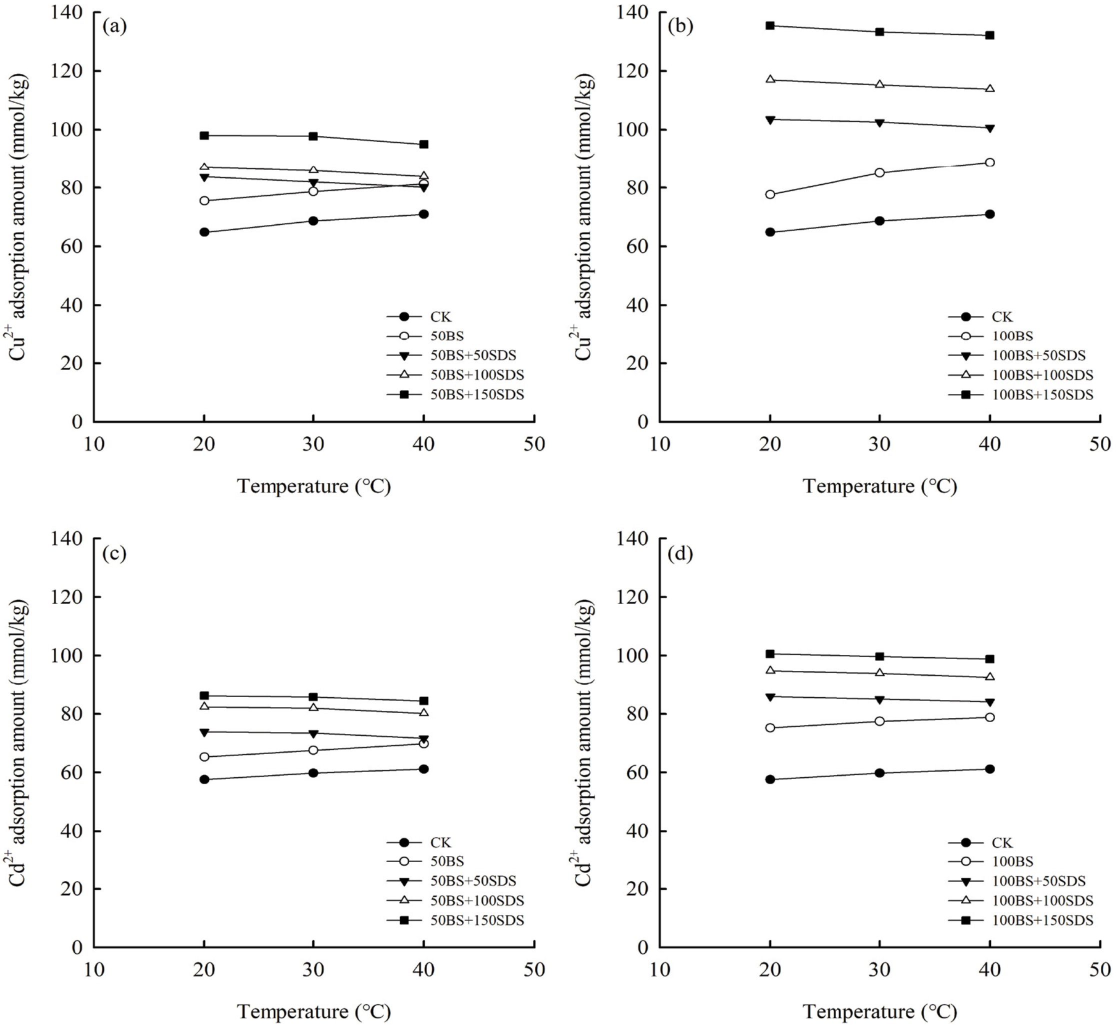

Fig. 3. Effect of temperature on Cu^{2+} and Cd^{2+} adsorption on different modified sierozems.

changed from 20°C to 40°C, the adsorption rates of Cu^{2+} increased by 9.37%, 7.61%, and 14.36%, while those of Cd^{2+} increased by 6.18%, 6.81% and 4.73% on CK, 50BS- and 100BS-modified sierozem, respectively. The adsorption rates of Cu^{2+} and Cd^{2+} on BS+SDS-modified sierozem decreased by 2.43%–4.42% and 2.74%–5.57%, respectively. With the increase of temperature, the adsorption capacity of Cu^{2+} and Cd^{2+} by CK- and BS-modified soils gradually increased, showing a positive temperature effect. However, the adsorption capacities of Cu^{2+} and Cd^{2+} onto BS+SDS-modified sierozem decreased with the increase of temperature, showing a negative effect of temperature increase.

The temperature effect of Cu^{2+} and Cd^{2+} adsorption shifted from positive to negative with the change if soil sample changed from CK and BS-modified sierozem to BS+SDS-modified sierozem. In other words, after SDS modification, the adsorption of BS-modified sierozem gradually shifted from an endothermic to an exothermic process. In comparison with Cd^{2+}, the adsorption capacity of Cu^{2+} on BS-modified soil samples remarkably increased with increasing temperature, and the adsorption capacity of Cu^{2+} on BS+SDS-modified sierozem slightly decreased with increasing temperature. This finding was consistent with the results of Cd^{2+} adsorption by modified bentonite and yellow-brown soil [16,20].

3.3. Effect of pH on Cu^{2+} and Cd^{2+} adsorption

The adsorption changes of Cu^{2+} and Cd^{2+} on the tested samples in the pH range of 3–7 are shown in Fig. 4. As the pH value of the solution increased, the adsorption capacities of Cu^{2+} and Cd^{2+} in all samples increased, reaching the maximum value at pH = 7. In comparison with Cd^{2+}, the adsorption capacity of Cu^{2+} on BS- and BS+SDS-modified sierozem had a higher increase with the increase of pH. When pH value increased from 3 to 7, the adsorption rates of Cu^{2+} and Cd^{2+} on CK, BS- and BS+SDS-modified sierozems increased by 1.24%–3.54% and 1.05%–2.97%, respectively. With the increase in pH, the number of OH^- ions increased, which easily co-precipitated with Cu^{2+} and Cd^{2+} and then deposited on the sierozems surface [21,22].

3.4. Effect of ionic strength on Cu^{2+} and Cd^{2+} adsorption

When the ionic strength was in the range of 0.05–0.50 mol/L, the adsorption capacity of Cu^{2+} and Cd^{2+} on all

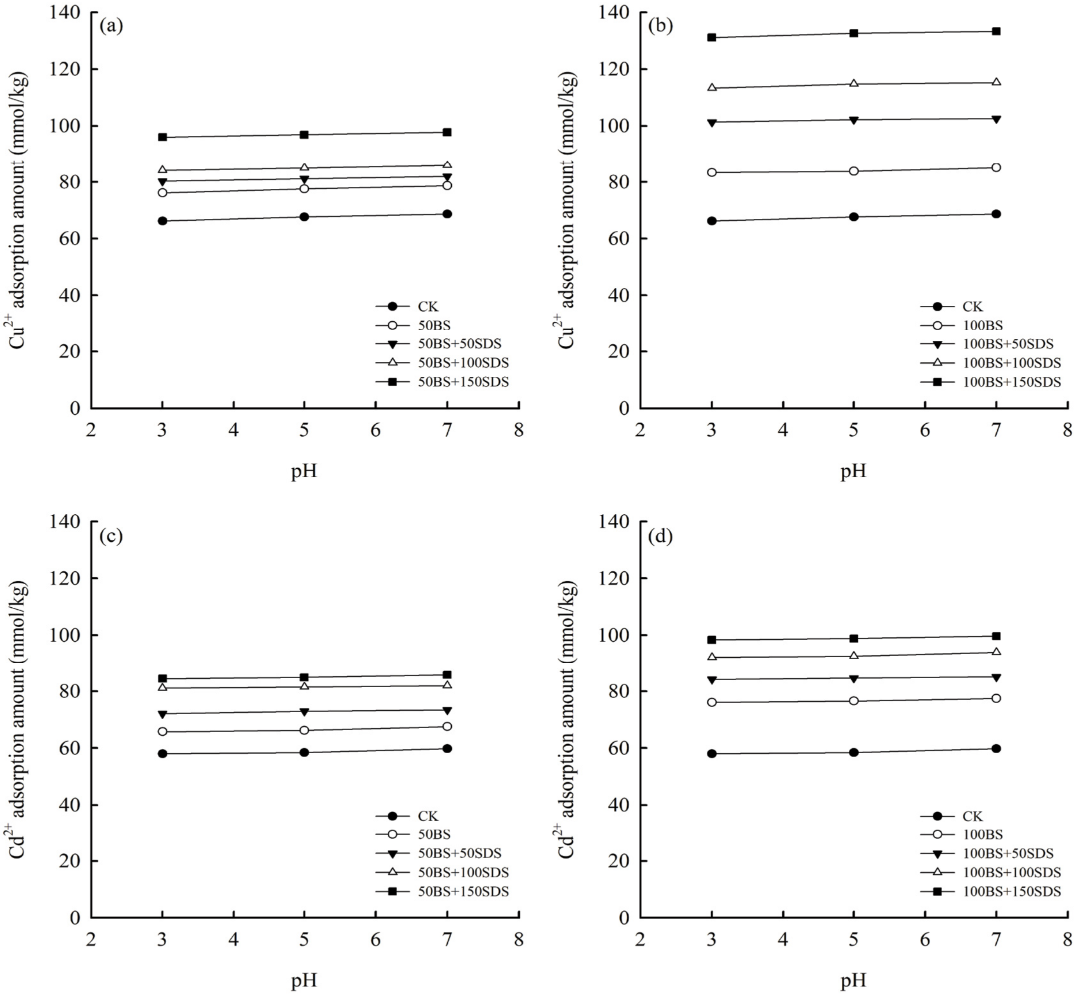

Fig. 4. Effect of pH on Cu^{2+} and Cd^{2+} adsorption on different modified sierozems.

the tested samples decreased with the increase of ionic strength (Fig. 5). When the ionic strength increased from 0.05 to 0.5 mol/L, the adsorption capacities of Cu^{2+} and Cd^{2+} on all the tested samples decreased by 3.05%–6.87% and 3.70%–7.17%, respectively. The amplitude of Cu^{2+} and Cd^{2+} adsorption decreased with increasing ionic strength in the order of CK > BS-modified sierozem > BS+SDS-modified sierozem, indicating that sierozem modified by BS and SDS can reduce the influence of ionic strength. In comparison with Cd^{2+}, with the increase of ionic strength, the adsorption capacity of Cu^{2+} in different modified samples decreased less. With the increase in ionic strength, the interaction between ions in the system was enhanced, and the decrease in the ion activity coefficient resulted in the decreased effective concentration of Cu^{2+} and Cd^{2+} [23].

3.5. Thermodynamic characteristics of Cu^{2+} and Cd^{2+} adsorption

The apparent thermodynamic parameters of Cu^{2+} and Cd^{2+} adsorption on each tested sample were calculated and listed in Table 2. The apparent free energy change ΔG of Cu^{2+} and Cd^{2+} adsorption at 20°C and 40°C was negative, indicating that the adsorption of Cu^{2+} and Cd^{2+} on all the tested samples were spontaneous. From CK to BS-modified sierozem, and then to BS+SDS-modified sierozem, negative ΔG was observed at 20°C and 40°C, showing a consistent change sequence with the adsorption strength parameter *b*. The ΔG values in the same soil samples were $-\Delta G40 > -\Delta G20$, indicating that with the increase of temperature, the spontaneity of Cu^{2+} and Cd^{2+} adsorption was enhanced.

The apparent enthalpy change ΔH values of Cu^{2+} and Cd^{2+} adsorption on CK and BS-modified sierozem were all positive, indicating that the adsorption of Cu^{2+} and Cd^{2+} was endothermic, and temperature rise enhanced the adsorption. The apparent enthalpy change ΔH of Cu^{2+} and Cd^{2+} adsorption on BS+SDS-modified sierozems were all negative, indicating that the adsorption of Cu^{2+} and Cd^{2+} was exothermic, and the temperature decrease enhanced the adsorption. These ΔH values were completely consistent with the conclusion in temperature effect and mutually verified. The ΔS values of all the tested samples were positive, indicating that the surface disorder of adsorption system was large. The adsorption of Cu^{2+} and Cd^{2+} on CK and BS-modified sierozem was spontaneous, endothermic, and entropy-increasing,

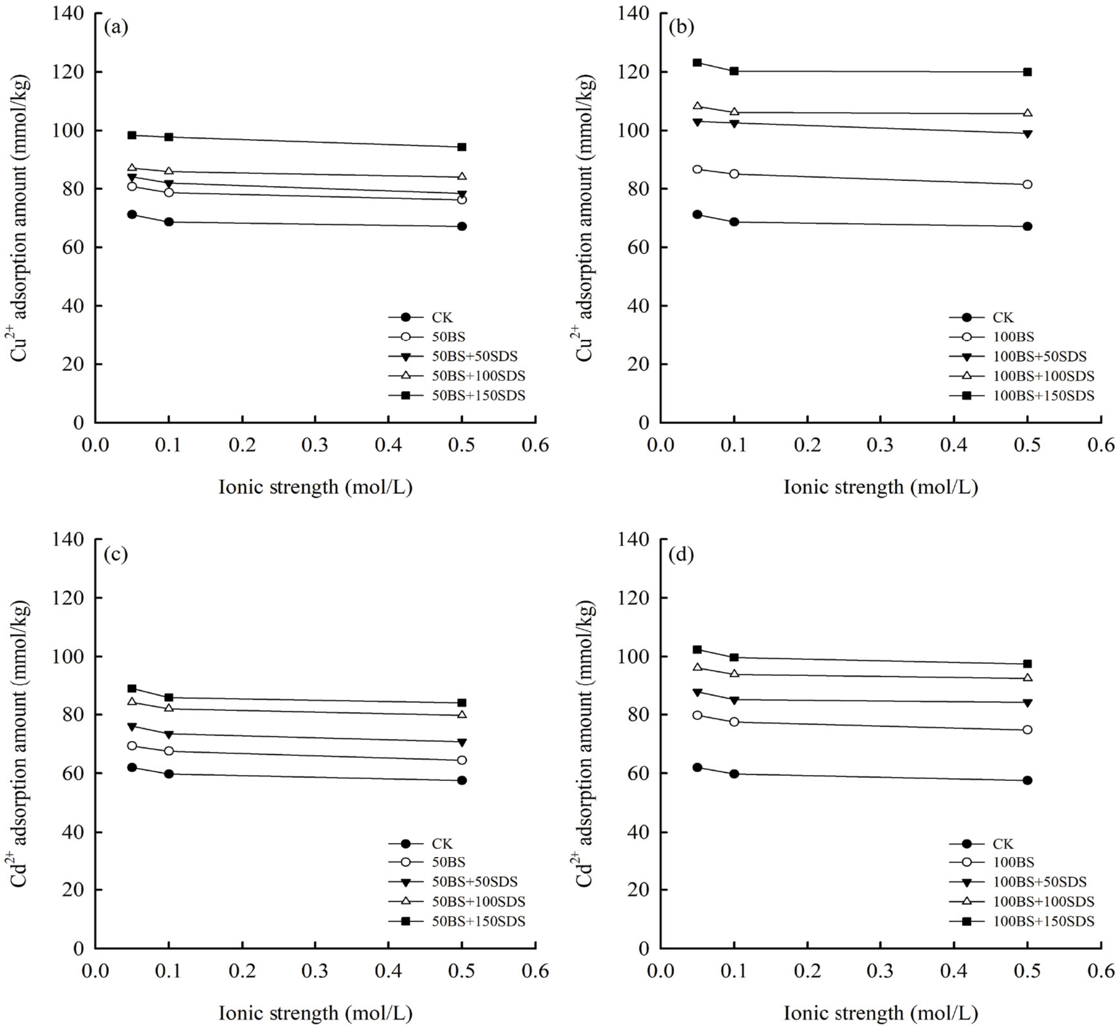

Fig. 5. Effect of ionic strength on Cu^{2+} and Cd^{2+} adsorption on different modified sierozems.

Table 2
Langmuir and thermodynamic parameters of Cu^{2+} and Cd^{2+} adsorption on different modified sierozems

Treatments		20°C		40°C			
		b	ΔG (kJ/mol)	*b*	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)
Cu^{2+}	CK	593.15	–15.55	610.56	–16.69	1.10	53.32
	50BS	573.26	–15.47	585.03	–16.58	0.77	52.97
	50BS+50SDS	472.18	–15.00	462.21	–15.97	–0.81	51.01
	50BS+100SDS	465.20	–14.96	455.35	–15.93	–0.80	50.89
	50BS+150SDS	448.83	–14.88	440.16	–15.84	–0.73	50.60
	100BS	372.36	–14.42	378.03	–15.44	0.58	49.34
	100BS+50SDS	290.43	–13.82	286.05	–14.72	–0.58	47.03
	100BS+100SDS	229.17	–13.24	226.00	–14.11	–0.53	45.07
	100BS+150SDS	183.68	–12.70	181.21	–13.53	–0.51	43.23
Cd^{2+}	CK	421.47	–14.72	436.40	–15.82	1.33	54.77
	50BS	391.46	–14.60	400.63	–15.60	0.88	52.65
	50BS+50SDS	366.71	–14.38	357.64	–15.30	–0.95	45.83
	50BS+100SDS	320.52	–14.06	313.53	–14.96	–0.84	46.28
	50BS+150SDS	289.75	–13.80	284.15	–14.70	–0.74	45.88
	100BS	258.42	–13.53	263.08	–14.50	0.68	48.03
	100BS+50SDS	249.32	–13.44	245.28	–14.32	–0.62	44.25
	100BS+100SDS	170.40	–12.52	167.87	–13.33	–0.57	41.27
	100BS+150SDS	167.30	–12.47	164.95	–13.29	–0.54	41.45

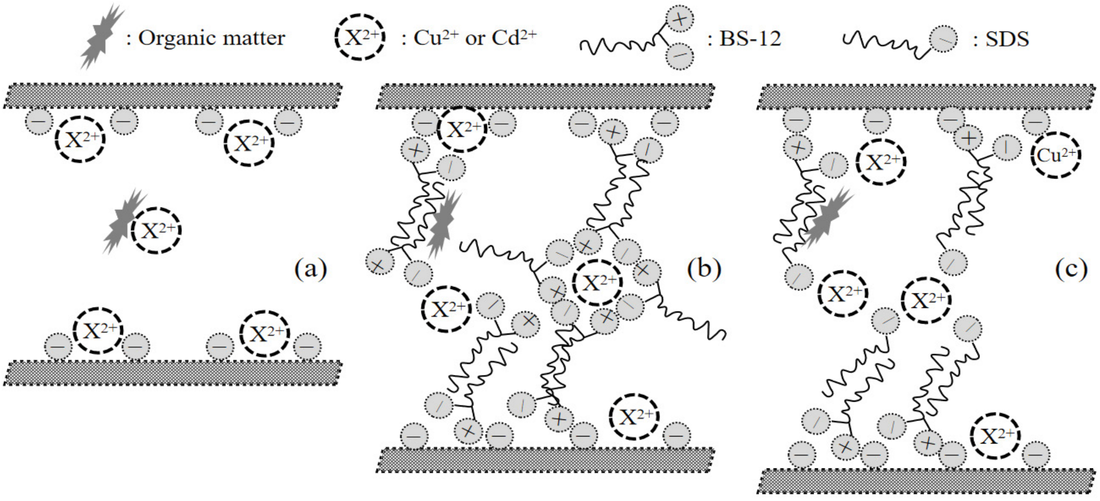

Fig. 6. Adsorption mechanism of Cu^{2+} and Cd^{2+} on CK (a), BS-modified (b), and BS+SDS-modified sierozems (c).

but that on BS+SDS-modified sierozem was a spontaneous, exothermic, and entropy-increasing process.

In addition, from CK to BS modification and then to BS+SDS modification, –ΔG and ΔS values gradually decreased, and ΔH gradually changed from positive to negative values. This finding indicates that after modification with BS and SDS, the adsorption of Cu^{2+} and Cd^{2+} on sierozem changed gradually from endothermic to exothermic. Therefore, the adsorption mechanism greatly changed. The result was similar to the thermodynamic parameters of Cd^{2+} adsorption by modified bentonite [20,24].

When sierozem was modified by BS, BS could easily combined with the negative charge sites on the outer surface of the sierozem by the positive charge group $–N^+$ end or the organic matter on sierozem by the long carbon chains of BS (Fig. 6). Cu^{2+} and Cd^{2+} could be adsorbed by negative charge points such as the carboxyl group of BS-modified sierozem and residual negative charge of sierozem by ion exchange. Moreover, Cu^{2+} and Cd^{2+} could form a complex with the lone electron pair atoms on the carboxyl group of BS-modified sierozems, making the q_m of Cd^{2+} and Cu^{2+} in BS-modified sierozem higher than that of CK [25,26]. The temperature effect of Cd^{2+} and Cu^{2+} adsorption on CK and BS-modified sierozem enhanced. Therefore, Cu^{2+} and Cd^{2+} were mainly adsorbed by surface complexation and ion exchange by CK and BS-modified sierozems. When SDS was modified on BS-modified sierozem, SDS was mainly combined with organic phase on the surface of BS-modified sierozem by their long carbon chains in the form of hydrophobic bonds. Then, the negative charge end extended outward [27], thus increasing the negative charge adsorption points on the surface of BS+SDS-modified sierozem [28]. The adsorption capacities of Cu^{2+} and Cd^{2+} on BS+SDS-modified sierozems were further enhanced via electrostatic attraction. Therefore, the temperature effect of Cu^{2+} and Cd^{2+} adsorption on BS+SDS-modified sierozems had a negative effect.

According to the above analysis, sierozem can adsorb Cu^{2+} and Cd^{2+} by ion exchange, surface complexation, and electrostatic attraction. However, the adsorption capacity of Cu^{2+} in sierozem was higher than that of Cd^{2+}. This parameter was determined based on the properties of the two metal ions themselves and the adsorption form of the metal ions in sierozem. For electrostatic attraction adsorption, high ion charge and small ion radius resulted in strong attraction between positive and negative charges [29]. Both Cu^{2+} and Cd^{2+} are divalent cations with the same number of charges, and metal ions are usually present in aqueous solutions as hydrated ions. However, the radius of hydrated ions of Cu^{2+} (0.419 nm) is smaller than that of Cd^{2+} (0.426 nm). Hence, the negative charge adsorption point has a stronger adsorption affinity for Cu^{2+} [30]. With the increase of the SDS modification proportion of BS+SDS-modified sierozem, the adsorption point of negative charge on the surface increased. In comparison with Cd^{2+}, Cu^{2+} in the solution was more easily adsorbed on the surface of BS+SDS-modified sierozem by electrostatic attraction. Hence, Cu^{2+} had a better directional distribution on the surface of BS+SDS-modified sierozem.

4. Conclusion

- The adsorption isotherm of Cu^{2+} and Cd^{2+} on different samples could be well fitted by the Langmuir model. The adsorption capacities of Cu^{2+} and Cd^{2+} on different modified sierozems were in the order of BS+150SDS > B S+100SDS > BS+50SDS > BS > CK. In comparison with Cd^{2+}, the adsorption capacity of Cu^{2+} on the same modified sierozem was high.
- The temperature effect on Cu^{2+} and Cd^{2+} adsorption changed from positive on CK and BS-modified sierozem to negative on BS+SDS-modified sierozem. The adsorption capacity of Cu^{2+} and Cd^{2+} on all tested samples increased with the increase of pH. The increase of ionic strength reduced the adsorption of Cu^{2+} and Cd^{2+} on different modified sierozems.
- Based on the thermodynamic parameters, the adsorption of Cu^{2+} and Cd^{2+} was a spontaneous, entropy-increasing, and endothermic process on CK and BS-modified sierozem and a spontaneous, entropy-increasing, and exothermic process on BS+SDS-modified sierozem.

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Conflict of interests

The authors declare that they have no conflict of interest.

References

[1] X.Y. Xu, Y.M. Cai, Study on competitive absorption properties for heavy metal ions by modified zeolite, J. Geol., 34 (2010) 92–97.

[2] A. Alengebawy, S.T. Abdelkhalek, S.R. Qureshi, M.-Q. Wang, Heavy metals and pesticides toxicity in agricultural soil and plants: ecological risks and human health implications, Toxics, 9 (2021) 42–54.

[3] S. Bai, Agricultural and forestry wastes material as potential adsorbent for heavy metal ions from aqueous solutions: a review, Environ. Sci. Technol., 37 (2014) 94–98.

[4] S.D. Shen, J. Xu. Adsorption of Cu(II) and Zn(II) ions onto NaOH-modified grapefruit husk powder, Environ. Sci. Technol., 33 (2010) 115–119.

[5] J.A. Antonangelo, H. Zhang, Heavy metal phytoavailability in a contaminated soil of northeastern oklahoma as affected by biochar amendment, Environ. Sci. Pollut. Res., 26 (2019) 33582–33593.

[6] I.I. Mokwenye, P.N. Diagboya, B.I. Olu-Owolabi, I.O. Anigbogu, H.I. Owamah, Immobilization of toxic metal cations on goethite-amended soils: a remediation strategy, J. Appl. Sci. Environ. Manage., 20 (2016) 436–443.

[7] M. Qaswar, Y. Liu, J. Huang, K. Liu, M. Mudasir, Z. Lv, H. Hou, X. Lan, J. Ji, A. Waqas, D. Li, H. Zhang, Soil nutrients and heavy metal availability under long-term combined application of swine manure and synthetic fertilizers in acidic paddy soil, J. Soil Sediment., 20 (2020) 2093–2106.

[8] Y. Liang, J. He, S. Zhang, Q. Xia, Effects of exogenous organic matter on the migration of organic contaminants with different polarities in soil, Int. J. Environ. Sci. Technol., 15 (2021) 203–214.

[9] C.R. Xie, Z.W. Wang, J.M. Zhu, X.L. Ma, Q.P. Zhang, Y.J. Wang, Adsorption of lead and copper from aqueous solutions on biochar produced from walnut green husk, Acta Sci. Circum., 36 (2016) 1190–1198.

[10] L.R. Varalakshmi, A.N. Ganeshamurthy, Phytotoxicity of cadmium in radish and its effects on growth, yield, and cadmium uptake, Commun. Soil Sci. Plant Anal., 44 (2013) 1444–1456.

[11] L.Z. Zhu, S. Feng, Synergistic solubilization of polycyclic aromatic hydrocarbons by mixed anionic-nonionic surfactants, Chemosphere, 53 (2003) 459–467.

[12] Z.-T. Liu, M. Xu, Z.-L. Lu, G.-Y. Zhang, W. Jin, Preparation and characterization of HDTMA-attapulgite and adsorption behavior to hexachlorocyolohexane, Chin. Environ. Sci., 30 (2010) 1602–1607.

[13] S.J. Zhan, S.L. Tian, J. Long, P. Ning, Sorption behavior of reversible cationic surfactant on bentonite, Chin. Environ. Sci., 34 (2014) 1831–1837.

[14] H. Ren, J. Jiang, D. Wu, Z. Gao, Y. Sun, C. Luo, Selective adsorption of Pb(II) and Cr(VI) by surfactant-modified and unmodified natural zeolites: a comparative study on kinetics, equilibrium, and mechanism, Water Air Soil Pollut., 227 (2016) 101–113.

[15] T. Xie, W.B. Li, Z.F. Meng, H.Y. Lu, S. Ren, Y. Sambath, Studies on Cr(VI) and Cd^{2+} adsorption onto bentonite modified by a BS-12+DTAB complex, J. Agro-Environ. Sci., 36 (2017) 1778–1786.

[16] W. Liu, Y. Zhang, Z.F. Meng, W.B. Li, S. Ren, Effect of amphoteric-anionic surfactant combined modification on Cd^{2+} adsorption of yellow brown soil, Chin. Environ. Sci., 37 (2017) 4620–4629.

[17] S.B. Bu, Z.F. Meng, Y. Sambath, 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) 311–319.

[18] W.B. Li, Z. Liu, Z.F. Meng, S. Ren, S.E. Xu, Y. Zhang, M.Y. Wang, Composite modification mechanism of cationic modifier to amphoteric modified kaolin and its effects on surface characteristics, Int. J. Environ. Sci. Technol., 13 (2016) 2639–2648.

[19] W.B. Li, J. Xie, H.Y. Deng, H.X. He, L. Zhu, L. Kang, W. Liu, Z.F. Meng, Effect of addition of different compositely modified amphipathic maifanites on Cu^{2+} adsorption by purple soil, J. Agro-Environ. Sci., 38 (2019) 863–870.

[20] J.T. Wang, Z.F. Meng, Y.T. Yang, S.Y. Yang, B. Li, L.L. Ma, S.E. Xu, Effect of SDS on the adsorption of Cd^{2+} onto amphoteric modified bentonites, Environ. Sci., 35 (2014) 2596–2603.

[21] R.K. Xu, S.C. Xiao, X. Jiang, J.J. Wu, D. Xie, Effect of pH on competitive adsorption of Cu(II) and Pb(II) on variable charge soils, Acta Pedol. Sinica, 43 (2006) 871–874.

[22] Y.G. Chen, W.M. Ye, X.M. Yang, F.Y. Deng, Y. He, Effect of contact time, pH, and ionic strength on Cd(II) adsorption from aqueous solution onto bentonite from Gaomiaozi, China, Environ. Earth Sci., 64 (2011) 329–336.

[23] X.L. Li, W.B. Li, H.Y. Deng, T. Li, D. Wang, Enhanced adsorption of Cu^{2+} on purple soil by amphoteric-modified materials, Desal. Water Treat., 196 (2020) 150–158.

[24] B.I. Olu-Owolabi, A.H. Alabi, E.I. Unuabonah, P.N. Diagboya, L. Böhm, R.A. Düring, Calcined biomass-modified bentonite clay for removal of aqueous metal ions, J. Environ. Chem. Eng., 4 (2016) 1376–1382.

[25] Z.F. Meng, Y.P. Zhang, G.D. Wang, Sorption of heavy metal and organic pollutants on modified soils, Pedosphere, 17 (2007) 235–245.

[26] Z.F. Meng, Y.P. Zhang, Z.Q. Zhang, Simultaneous adsorption of phenol and cadmium on amphoteric modified soil, J. Hazard. Mater., 159 (2008) 492–498.

[27] Y.H. Liu, Z.F. Meng, J.F. Bai, P.X. Qin, P.Y. Zheng, Y. Ji, Adsorption and desorption of Cd^{2+} on Lou soil modified with a mixture of amphoteric and anionic modifiers, Acta Sci. Circum., 30 (2010) 2011–2016.

[28] J.B. Zhou, P.X. Wu, N.W. Zhu, Z. Dang, Adsorption of Cu^{2+} and Cd^{2+} by SDS modified montmorillonite, Acta Sci. Circum., 30 (2010) 88–96.

[29] Y.R. Li, P. Bai, Y. Yan, W.F. Yan, W. Shi, R.R. Xu, Removal of Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} from aqueous solution by synthetic clinoptilolite, Microporous Mesoporous Mater., 273 (2019) 203–211.

[30] J.J. Liu, X.W. Tang, Y. Wang, Competitive adsorption behavior and mechanism of loess towards Pb(II), Cu(II) and Cd(II), Chin. J. Geothch. Eng., 36 (2014) 327–334.