

## Adsorption difference of Cu<sup>2+</sup> on the compositely modified amphipathic maifanites

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### ABSTRACT

To determine the effect of compositely modified amphipathic clay on Cu<sup>2+</sup> adsorption, 50% and 100% cation exchange capacity (CEC) of anionic polyacrylamide (PA in the modified amphipathic maifanite (M<sub>50x</sub>)), citric acid (CA), ethylenediaminetetraacetic acid (ED in M<sub>50x</sub>), and sodium dodecyl sulfate (SD in M<sub>50x</sub>) were used to modify the 50% CEC of dodecyl dimethyl betaine (BS-12 or BS)-modified maifanite (M<sub>50BS</sub>) and form four types of compositely modified amphipathic maifanite (M<sub>50x</sub>), such as M<sub>50BS/PA</sub> (including M<sub>50BS/50PA</sub> and M<sub>50BS/100PA</sub>; the same goes for the other samples), M<sub>50BS/CA</sub>, M<sub>50BS/ED</sub> and M<sub>50BS/SD</sub>. The adsorption and thermodynamic characteristics of Cu<sup>2+</sup> on the various compositely modified M<sub>50BS</sub> were investigated by using the batch method, and the adsorption difference in the pH value, temperature, and ion strength were discussed. The results showed that (1) the adsorption isotherms of Cu<sup>2+</sup> on the test samples were all “L” type and combined with the Langmuir model. The maximum adsorption amount of Cu<sup>2+</sup> on the different samples changed between 109.09 and 200.87 mmol/kg and presented the trend M<sub>50BS/PA</sub> > M<sub>50BS/CA</sub> > M<sub>50BS/SD</sub> > M<sub>50BS/ED</sub> > M<sub>50BS</sub> > M<sub>BS</sub>. M<sub>50BS/PA</sub> modified by 100% CEC of the composite modifier obtained superior Cu<sup>2+</sup> adsorption, and the adsorption amount of Cu<sup>2+</sup> was 1.10–1.20 times higher than that of M<sub>BS</sub> modified by 50% CEC of the composite modifier. (2) In the range of 20°C to 40°C, the adsorption amount of Cu<sup>2+</sup> in the tested samples increased with the increase in temperature, except for M<sub>50BS/PA</sub> and M<sub>50BS/SD</sub>, and the increasing range was 7.56%–16.79%. (3) Within the pH range of 3 to 5, the Cu<sup>2+</sup> adsorbed by each test sample increased with increasing pH value. The adsorption amount of Cu<sup>2+</sup> on the tested maifanites (except M<sub>50BS</sub>) decreased with increasing ionic strength, wherein the best amount was at 0.01 mol/L. (4) The adsorption of Cu<sup>2+</sup> on the tested maifanites was a spontaneous, endothermic (except M<sub>BS/PA</sub> and M<sub>50BS/SD</sub>), and entropic-adding process.

**Keywords:** Composite modification; Amphipathic maifanite; Cu<sup>2+</sup>; Adsorption amount

### 1. Introduction

The discharge of industrial wastes and unreasonable application of pesticides and fertilizers caused serious heavy metal pollution in the soil [1,2], thereby making pollution

management an urgent problem to be solved [3,4]. Clay minerals are not only important soil components that can fix heavy metal ions but also materials with properties that can change the existing forms of heavy metal ions in the soil to reduce their mobility and toxicity [5,6]. Therefore, studies should focus on reducing the activity of pollutants and

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improving the soil environment by using clay minerals to remediate the heavy metal pollution in the soil.

Numerous scholars have studied and applied clay minerals due to their advantages of cost-effectiveness, easy availability, and good adsorption performance [7,8]. Clay minerals commonly used to repair heavy metal pollution in the soil include maifanite, zeolite, kaolinite, sepiolite, vermiculite, and illite [6]. Studies showed that zeolite can change the morphology of heavy metals to a certain extent [9], whereas montmorillonite can reduce the active content of Cu and Zn in sludge and the absorption amount of heavy metals via ryegrass [10], and natural zeolite can effectively reduce the heavy metal content absorbed by plants from the soil [11]. The adsorption study of heavy metal ions using natural clay minerals has achieved good progress. The adsorption capacity of clay minerals could be improved by altering clay minerals with modifiers [12]. Scholars had used cationic, anionic and amphoteric modifiers to adjust various clay minerals, and the modified clay minerals presented strong adsorption capacities for heavy metals [13–15]. However, a cationic modifier is unsuitable for soil improvement applications because of its high price and strong sterilization. An amphoteric surfactant features both positively and negatively charged hydrophilic groups and hydrophobic carbon chains, indicating good environmental compatibility [16]. The use of amphoteric surfactants to modify clay minerals can effectively enhance their adsorption capacity to heavy metal cations. Dodecyl dimethyl betaine (BS-12 or BS)-modified Lou soil was used by Meng et al. [17] to adsorb  $\text{Cd}^{2+}$ , wherein the adsorption amount reached 1.3–1.8 times higher than that of unmodified soil. The maximum adsorption amount of  $\text{Cd}^{2+}$  on yellow-brown soil modified by BS-12 + sodium dodecyl sulfate (SDS, SD in labeled modified samples) was 4.85–6.40 times higher than that of unmodified yellow-brown soil [18].

Copper is both a heavy metal element and a nutrient element. Therefore, the remediation of  $\text{Cu}^{2+}$  pollution by using clay minerals and modified clay materials has become an important research topic in recent years. Cu is mainly adsorbed by clay minerals in the soil, especially in soil with low organic content [19]. Gao and Rong [20] observed that the adsorption capacity of maifanite to  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$  increased successively, but the adsorption selectivity and stability of heavy metal ions on natural clay minerals were poor. Hence, the adsorption amount was low. Scholars proposed the idea of using amphoteric modified soil to adsorb heavy metals and revealed that BS-12-modified clay maintained strong adsorption capacity to heavy metals [21,22]. Apart from being extremely abundant and inexpensive, maifanites show good adsorption, dissolution, mineralization, and biological activity. Maifanites cannot introduce new heavy metal pollutants into the soil and thus avoids the risk of secondary pollution [23,24]. This material is ideal for the adsorption of clay minerals. If different types of composite modifiers are used to modify amphoteric maifanites, then they can improve not only the adsorption capacity of maifanites for heavy metal pollution but also select the composite modification mode and addition proportion for better adsorption effect. However, the studies focusing on this aspect are limited. In this study, anionic polyacrylamide (PA) and sodium dodecyl sulfate (SD) with negatively

charged characteristics were selected for electrostatic attraction, whereas ethylenediaminetetraacetic acid (ED) and citric acid (CA) were used for complexation or chelation. These composite modifiers are all safe to use and produce no secondary pollution. Hence, they were used to modify amphipathic maifanites with modification proportions of 50% and 100%. The adsorption effects of  $\text{Cu}^{2+}$  on different compositely modified amphoteric maifanites were studied. In addition, the adsorption differences under different environmental conditions, such as temperature, pH value, and ionic strength were discussed to provide a reference for the efficient adsorption of compositely modified amphipathic maifanites in the remediation of copper-contaminated soil.

## 2. Materials and methods

### 2.1. Materials

Maifanite (M), the tested clay mineral, was purchased from Qiqihar, Inner Mongolia. This mineral features a 200 mesh particle size, 8.60 pH, 180.24 mmol/kg cation exchange capacity (CEC), 5.02  $\text{m}^2/\text{g}$  specific surface area, and 2.52 mg/kg  $\text{Cu}^{2+}$  content.

*Experimental modifiers:* The amphoteric modifier was BS-12 or BS (analytical reagent, produced by Tianjin Xingguang Preparation Factory, Tianjin City, China). The composite modifiers comprised anionic polyacrylamide (APAM) (chemical reagent, Chengdu Kelon Chemical Reagent Factory, Sichuan province, China), CA (analytical reagent, Chengdu Kelon Chemical Reagent Factory, Sichuan province, China), ethylene diamine tetraacetic acid (EDTA) (analytical reagent, Chengdu Kelon Chemical Reagent Factory, Sichuan province, China) and SDS (analytical reagent, Tianjin Dingshengxin Chemical Co. Ltd., Tianjin City, China). Fig. 1 shows the molecular formula of each modifier.

$\text{Cu}^{2+}$  solution was used as the pollutant and prepared by using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (analytical reagent) purchased from Chengdu Kelon Chemical Reagent Factory (Sichuan province, China).

### 2.2. Preparation of compositely modified amphipathic maifanite

Amphipathic maifanite ( $M_{50\text{BS}}$ ) was prepared by using the wet method [25]. A certain weight of maifanite was prepared for modification, slowly added to the prepared BS-12 solution at a soil/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 maifanite  $M_{50\text{BS}}$  could be obtained after washing with deionized water thrice to ensure that the pH of the modified materials exhibited minimal changes. Amphipathic maifanite was dried at 60°C for 12 h and then passed through a 0.25 mm sieve.

The composite modification method was the same as amphipathic modification. The dosage of amphoteric and composite modifiers was calculated by using Eq. (1) [26].

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

where  $W$  refers to the quality of modifier, g;  $m$  denotes the mass of maifanite, g; CEC represents the CEC of maifanite, mmol/kg;  $M$  specifies the molar mass of the modifier,



$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (5)$$

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. Isothermal adsorption characteristics of $\text{Cu}^{2+}$ on tested samples

The  $\text{Cu}^{2+}$  adsorption isotherms of the different compositely modified amphipathic maifanites determined at the experimental temperature was  $30^\circ\text{C}$  (Fig. 2). The adsorption isotherm all presented the “L” type, which proved that the Langmuir model was applicable to describe the adsorption of  $\text{Cu}^{2+}$  by various compositely modified amphipathic maifanites. Table 1 shows the fitting results of the adsorption isotherm via the Langmuir model.

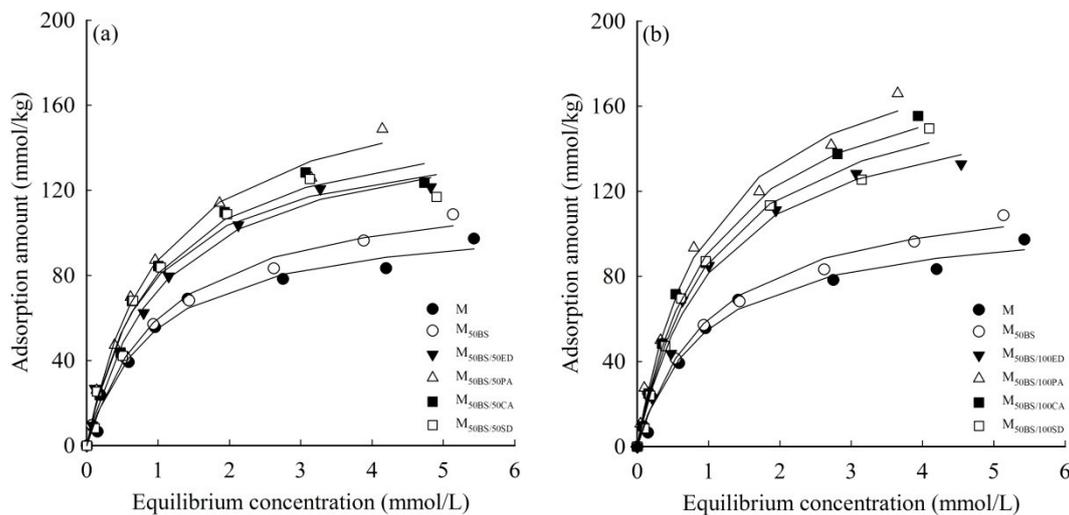


Fig. 2. Adsorption isotherms of  $\text{Cu}^{2+}$  on different compositely modified maifanites.

Table 1  
Langmuir fitting parameters of  $\text{Cu}^{2+}$  adsorption isotherms

Compositely modified amphipathic maifanites	Correlation coefficients/ $r$	Standard deviations/ $S$	$q_m$ (mmol/kg)	$b$ (L/mmol)
M	0.9905 <sup>a</sup>	5.12	109.09	1.03
$M_{50BS}$	0.9927 <sup>a</sup>	4.92	124.53	0.92
$M_{50BS/50ED}$	0.9929 <sup>a</sup>	5.90	154.97	0.90
$M_{50BS/50PA}$	0.9956 <sup>a</sup>	5.36	177.02	0.98
$M_{50BS/50CA}$	0.9917 <sup>a</sup>	6.77	160.08	1.02
$M_{50BS/50SD}$	0.9870 <sup>a</sup>	8.19	150.56	1.12
$M_{50BS/100ED}$	0.9959 <sup>a</sup>	4.91	170.19	0.92
$M_{50BS/100PA}$	0.9952 <sup>a</sup>	6.15	200.87	1.00
$M_{50BS/100CA}$	0.9964 <sup>a</sup>	5.10	190.92	0.93
$M_{50BS/100SD}$	0.9957 <sup>a</sup>	5.30	180.52	0.92

<sup>a</sup>Indicates significance at the  $p = 0.01$  level ( $r = 0.765$  at  $p = 0.01$  when the degrees of freedom  $f = 8$ ).

Under the same equilibrium concentration, the adsorption capacity of  $\text{Cu}^{2+}$  presented the trend  $M_{50BS/PA} > M_{50BS/CA} > M_{50BS/SD} > M_{50BS/ED} > M_{50BS} > M$ . In addition, under the same modification mode, the adsorption capacity of  $\text{Cu}^{2+}$  could be enhanced by the 100% composite modification ratio. The maximum adsorption amount ( $q_m$ ) of  $\text{Cu}^{2+}$  for each compositely modified amphipathic maifanite was between 109.09 and 200.87 mmol/kg and maintained a trend of  $M_{50BS/100PA} > M_{50BS/100CA} > M_{50BS/100SD} > M_{50BS/50PA} > M_{50BS/100ED} > M_{50BS/50CA} > M_{50BS/50ED} > M_{50BS/50SD} > M_{50BS} > M$ , consistent with the results of the adsorption capacity shown in Fig. 1.  $q_m$  of  $\text{Cu}^{2+}$  on different compositely modified amphipathic maifanites was significantly higher than that of M, and the adsorption amount of  $\text{Cu}^{2+}$  on M was increased by 1.14%–1.84% with the amphipathic and composite-amphipathic modification.

#### 3.2. Effect of temperature on $\text{Cu}^{2+}$ adsorption

The changes in adsorption of  $\text{Cu}^{2+}$  on the compositely modified amphipathic maifanites were determined

in the range of 20°C–40°C (Fig. 3). The results showed that the adsorption amount of  $\text{Cu}^{2+}$  on the different samples increased with the increase in temperature, except for  $M_{50\text{BS}/\text{PA}}$  and  $M_{50\text{BS}/\text{SD}}$  thereby indicating a positive temperature effect. From 20°C to 40°C, the adsorption amount of  $\text{Cu}^{2+}$  on M increased by 7.56% and by 8.49%–16.50% in  $M_{50\text{BS}}$ ,  $M_{50\text{BS}/\text{CA}}$  and  $M_{50\text{BS}/\text{ED}}$  thus increasing the amplitude (shown in brackets) rank order to  $M_{50\text{BS}}$  (16.79%) >  $M_{50\text{BS}/100\text{CA}}$  (16.50%) >  $M_{50\text{BS}/50\text{CA}}$  (13.13%) >  $M_{50\text{BS}/100\text{ED}}$  (9.15%) >  $M_{50\text{BS}/50\text{ED}}$  (8.49%). The above results were mainly due to the complexation or chelation of BS-12, CA, and EDTA to  $\text{Cu}^{2+}$ , thereby indicating a chemical process and an endothermic reaction. The adsorption amount of  $\text{Cu}^{2+}$  via  $M_{50\text{BS}/\text{PA}}$  and  $M_{50\text{BS}/\text{SD}}$  presented a negative effect with increasing temperature, and decreased by 3.96%–6.94% and 3.33%–5.79% respectively, because the electrostatic attraction of APAM and SDS to  $\text{Cu}^{2+}$  exhibited physical adsorption, and APAM showed a strong flocculation and precipitation effect on the hydrogen oxides formed by  $\text{Cu}^{2+}$  and  $\text{OH}^-$ , thus also indicating physical and exothermic reactions [29].

### 3.3. Effect of pH on $\text{Cu}^{2+}$ adsorption

Fig. 4 illustrates that the adsorption amount of  $\text{Cu}^{2+}$  on each compound maifanite increases with the increase in pH value in the range of pH 3–5. The adsorption amount of  $\text{Cu}^{2+}$  on  $M_{50\text{BS}}$  increased by 12.97%, and the amplification was 1.84 times higher than that of M. For 50% composite modification, the increased range of  $\text{Cu}^{2+}$  adsorption (as shown in the brackets) demonstrated the trend  $M_{50\text{BS}/50\text{ED}}$  (22.06%) >  $M_{50\text{BS}/50\text{PA}}$  (16.34%) >  $M_{50\text{BS}/50\text{CA}}$  (5.80%) >  $M_{50\text{BS}/50\text{SD}}$  (5.05%). Moreover, under 100% composite modification, the adsorption amount of  $\text{Cu}^{2+}$  on the different samples increased by 3.30%–26.52% and also showed an increasing trend for  $M_{50\text{BS}/\text{ED}}$  and  $M_{50\text{BS}/\text{PA}}$  because EDTA was more likely protonated under acidic condition, which was not conducive to its chelation with heavy metal ions [30], thus reducing the adsorption amount of  $\text{Cu}^{2+}$ . However, under acidic conditions, APAM was not conducive to electrostatic attraction to cationic heavy metals and reduced its flocculation precipitation to  $\text{Cu}^{2+}$ .

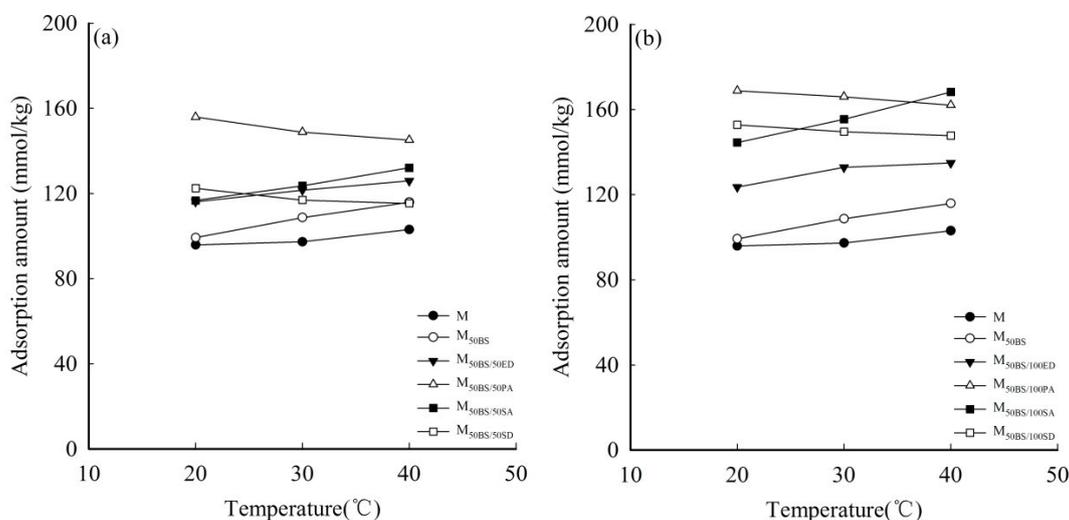


Fig. 3. Temperature effect of  $\text{Cu}^{2+}$  adsorption on the different samples.

Table 2  
Effect of ionic strength on  $\text{Cu}^{2+}$  adsorption

Samples	Adsorption amount (mmol/kg)		
	$I = 0.01 \text{ mol/L}$	$I = 0.1 \text{ mol/L}$	$I = 0.5 \text{ mol/L}$
M	$100.82a \pm 2.90$	$97.24a \pm 2.73$	$94.72a \pm 2.00$
$M_{50\text{BS}}$	$108.01a \pm 1.46$	$108.70a \pm 1.85$	$102.49a \pm 1.90$
$M_{50\text{BS}/50\text{ED}}$	$123.42a \pm 3.70$	$121.56a \pm 4.53$	$120.68a \pm 5.67$
$M_{50\text{BS}/50\text{PA}}$	$151.92a \pm 3.72$	$148.78ab \pm 3.64$	$136.17b \pm 2.55$
$M_{50\text{BS}/50\text{CA}}$	$126.10a \pm 19.60$	$123.60b \pm 6.54$	$123.11b \pm 0.45$
$M_{50\text{BS}/50\text{SD}}$	$122.41a \pm 5.91$	$116.87ab \pm 1.32$	$105.17b \pm 1.61$
$M_{50\text{BS}/100\text{ED}}$	$135.89a \pm 11.00$	$132.86a \pm 1.96$	$130.54a \pm 3.40$
$M_{50\text{BS}/100\text{PA}}$	$168.51a \pm 26.11$	$165.96a \pm 3.09$	$149.49a \pm 2.39$
$M_{50\text{BS}/100\text{CA}}$	$157.28a \pm 2.92$	$155.42a \pm 0.26$	$153.04a \pm 4.26$
$M_{50\text{BS}/100\text{SD}}$	$158.46a \pm 1.94$	$149.58b \pm 1.73$	$137.99c \pm 1.45$

### 3.4. Effect of ion strength on $\text{Cu}^{2+}$ adsorption

In the range of 0.01–0.1 mol/L, the adsorption amount of  $\text{Cu}^{2+}$  by M and each compound of maifanite (except  $M_{50\text{BS}}$ ) decreased with the increase in ion strength (Table 2). With the change in ionic strength, the reduction degree of each compound of maifanite totaled 2.22%–14.08% and was significantly reduced by  $M_{50\text{BS}/\text{PA}}$  and  $M_{50\text{BS}/50\text{SD}}$ . A significant difference was observed between ionic strength ( $I$ ) = 0.01 mol/L and  $I$  = 0.5 mol/L because the increase in  $\text{Na}^+$  in the solution would lead to the decreased electrostatic attraction of SDS and APAM to  $\text{Cu}^{2+}$  on maifanites, and subsequent decrease in the adsorption amount of  $\text{Cu}^{2+}$ .

### 3.5. Thermodynamic characteristics of $\text{Cu}^{2+}$ adsorption

Table 3 lists the thermodynamic parameters of  $\text{Cu}^{2+}$  adsorption of each sample. Under the temperatures of 20°C and 40°C, the apparent free energy changes ( $\Delta G$ ) in  $\text{Cu}^{2+}$  adsorption on all the tested materials were less than 0, thereby indicating the spontaneous adsorption of  $\text{Cu}^{2+}$ . This

spontaneity was stronger at 40°C under the same treatment. In addition to  $M_{50BS/PA}$  and  $M_{50BS/SD}$ , the apparent enthalpy change  $\Delta H$  was positive, thus proving that the adsorption process was an endothermic reaction, and the increase in temperature benefitted the adsorption of  $Cu^{2+}$ , consistent with the temperature effect in Fig. 3. The  $\Delta H$  of  $M_{50BS/PA}$  and  $M_{50BS/SD}$  on  $Cu^{2+}$  were less than 0, which coincided with the adsorption process of the physical electrostatic adsorption mechanism. The apparent entropy change  $\Delta S$  was all greater than zero, which explained the process of  $Cu^{2+}$  adsorption as an entropy increase reaction. This event mainly occurred due to the distribution of the maifanite surface by different modifiers.

Cationic exchange points existed on the electronegative surface of maifanite, and the adsorption of  $Cu^{2+}$  mainly relied on ion exchange and surface complexation [31]. This process was a chemical (endothermic) reaction, but the adsorption effect was weak. Hence, the adsorption presented a weak positive temperature effect.

Amphoteric modifier BS-12 contains both positively and negatively charged hydrophilic groups and hydrophobic

carbon chains. BS-12 modification with 50% CEC presented ion exchange mode on the surface of maifanite [32], which contained a cation exchange point. The positive charge of BS-12 combined with the negative charge on the surface of maifanite. Thus, the hydrophilic terminal negative charge and the hydrophobic carbon chain were exposed on the surface of the amphipathic maifanite. The adsorption of  $Cu^{2+}$  by amphipathic maifanite mainly depended on the complexation via the surface-modified BS-12 hydrophilic end to  $Cu^{2+}$ , ion exchange, and surface complex adsorption of maifanite itself to  $Cu^{2+}$ , thereby indicating a chemisorption process. Therefore, the modification of maifanite using BS-12 promoted the adsorption of  $Cu^{2+}$  by maifanite.

APAM and SDS exhibited strong electrostatic attraction to  $Cu^{2+}$ , thus indicating a physical reaction [22,29]. Therefore, composite modification via APAM and SDS promoted the adsorption of  $Cu^{2+}$  on amphoteric maifanite mainly by physical electrostatic adsorption, and the adsorption showed a negative temperature effect. EDTA and CA had strong complexation or chelation for  $Cu^{2+}$ , implying a chemical reaction [30,33]. Hence, the adsorption of  $Cu^{2+}$  via  $M_{50BS/ED}$  and  $M_{50BS/CA}$

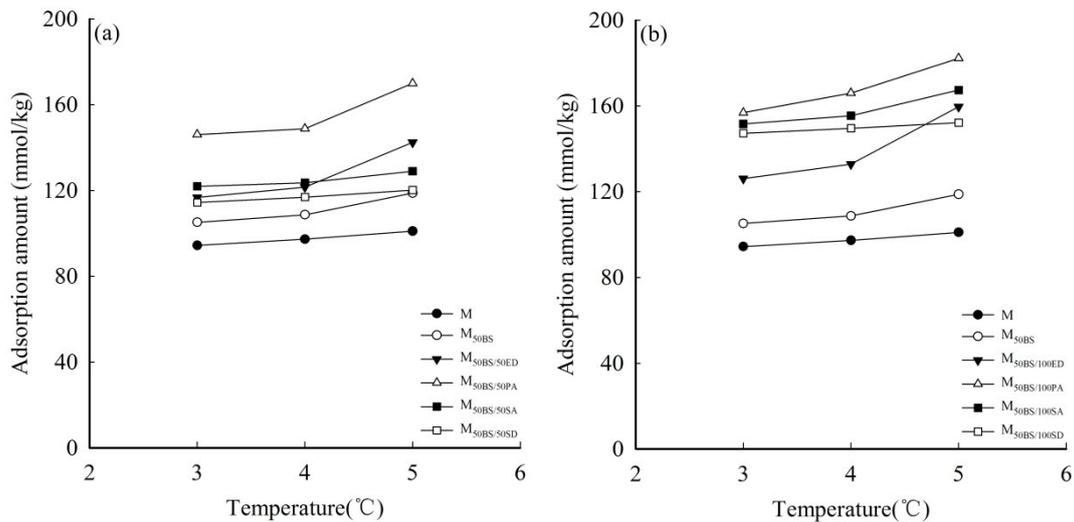


Fig. 4. pH effect of  $Cu^{2+}$  adsorption on different compositely modified maifanites.

Table 3  
Thermodynamic parameters of  $Cu^{2+}$  adsorption in different compositely modified maifanites

Composite modified maifanites	20°C			40°C		
	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/(mol K))	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/(mol K))
M	-16.87	2.78	67.04	-18.21	2.78	67.04
$M_{50BS}$	-16.42	5.92	76.22	-17.95	5.92	76.22
$M_{50BS/50PA}$	-16.91	-2.74	48.33	-17.88	-2.74	48.33
$M_{50BS/50CA}$	-16.74	4.71	73.18	-18.21	4.71	73.18
$M_{50BS/50ED}$	-16.47	3.11	66.78	-17.80	3.11	66.78
$M_{50BS/50SD}$	-17.22	-2.28	50.99	-18.24	-2.28	50.99
$M_{50BS/100PA}$	-16.88	-1.54	52.31	-17.92	-1.54	52.31
$M_{50BS/100CA}$	-16.48	5.83	76.09	-18.00	5.83	76.09
$M_{50BS/100ED}$	-16.46	3.34	67.54	-17.81	3.34	67.54
$M_{50BS/100SD}$	-16.69	-1.29	52.54	-17.75	-1.30	52.54

was remarkably improved compared with that obtained by M and  $M_{50BS'}$  and the adsorption showed a strong positive temperature effect.

#### 4. Conclusion

- The Langmuir model was suitable for describing the isotherm of  $Cu^{2+}$  adsorption for all the tested materials. The adsorption capacity all followed the trend  $M_{50BS/PA} > M_{50BS/CA} > M_{50BS/SD} > M_{50BS/ED} > M_{50BS} > M$ , and the 100% modification proportion of composite modifier enhanced the  $Cu^{2+}$  adsorption better.
- In the range of 20°C–40°C, except for  $M_{50BS/PA}$  and  $M_{50BS/SD}$ , the adsorption amount of  $Cu^{2+}$  on the compositely modified amphipathic maifanites increased with the increasing temperature, and the  $Cu^{2+}$  adsorption increased by 1.36–3.29 times higher than that from 20°C to 40°C.
- Within the range of pH 3–5, the adsorption amount of  $Cu^{2+}$  on each sample increased with the increase in pH value. In the  $I = 0.01$ – $0.1$  mol/L, the adsorption amount of  $Cu^{2+}$  on each sample (except  $M_{50BS}$ ) decreased with increasing ionic strength.
- The adsorption of  $Cu^{2+}$  by using each sample was spontaneous and exhibited an entropic-adding reaction. Except for  $M_{50BS/PA}$  and  $M_{50BS/SD}$  the adsorption of  $Cu^{2+}$  via other compositely modified amphoteric maifanites presented an endothermic reaction.

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