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Enhanced adsorption of Cu^{2+} on purple soil by amphoteric-modified materials

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ABSTRACT

To investigate the effect of adding amphoteric materials on Cu^{2+} adsorption of purple soil (P), we selected dodecyl betaine (BS-12) as the amphoteric modifier and modified bentonite (B), diatomite (D), activated carbon (C), maifanite (M), and active calcium silicate (S) using 100%BS-12 (as measured by the cation exchange capacity of the material) to obtain five kinds of amphoteric materials. Then, the amphoteric materials were added to P at the mass ratios of 1% and 2% to form 10 mixed soil samples of $1\%B_{100BS}$ and $2\%B_{100BS}$ (P mixed with 1% and 2% amphoteric modified B, respectively, the same below), $1\%D_{100BS}$ and $2\%D_{100BS}$, $1\%C_{100BS}$ and $2\%C_{100BS}$, $1\%M_{100BS}$ and $2\%M_{100BS}$, and $1\%S_{100BS}$ and $2\%S_{100BS}$ (with P as a contrast). Batch method was used to study the isothermal adsorption and thermodynamic characteristics of Cu^{2+} on different mixed soil samples as a function of different temperatures, pH, and ionic strengths. The following results were obtained. (1) The adsorption isotherms of Cu^{2+} on different mixed soil samples fitted well the Langmuir and Freundlich models, and the maximum adsorption amount (q_m) was between 89.12 and 137.16 mmol/kg, respectively. At the same addition ratio, the adsorption capacity of Cu^{2+} on tested soil samples showed the follow trend: $B_{100BS} > D_{100BS} > C_{100BS} > S_{100BS} > M_{100BS} > P$. Compared with 1% addition ratio, the adsorption amount was better under the addition ratio of 2%. (2) When the temperature increased from 20°C to 40°C, the adsorption amount of Cu^{2+} on all the mixed soil samples increased with rising temperature. The thermodynamic parameters indicated that the adsorption of Cu^{2+} on mixed soil samples was spontaneous, endothermic, and entropy increasing. (3) The adsorption amount of Cu^{2+} on the tested soil samples increased with the increase in pH from 3 to 5. With the increase in ionic strength, the adsorption amount of Cu^{2+} on all mixed soil samples initially increased and then decreased, and the peak value was at 0.1 mol/L.

Keywords: BS-12; Adsorbent material; Purple soil; Cu^{2+}; Adsorption capacity

1. Introduction

Under the influence of urbanization, soil pollution caused by heavy metals seriously restricts the efficient use of soil [1]. Adsorption is an important physical and chemical method that can not only reduce the concentration of heavy metal ions in the environment, but also enable their desorption and utilization; this process has a broad application prospect in the field of environmental pollution remediation [2]. Currently, various adsorbents have been applied to remove heavy metal ions [3]. Diatomite (D) and bentonite (B) have good adsorption effects on various heavy metal ions, and the adsorption capacity of B with the same quality is better than that of D [4]. Maifanite (M) could reduce the activity of Cu and Cd in contaminated soil; Cu^{2+} extraction by soil weak acid decreased from 37.36% to 15.07% [5]. However, its adsorption performance

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is uneven, modified adsorbents could considerably improve its adsorption capacity [6]. Modified materials are added to enhance the adsorption capacity of actual soils for pollutants; this process is important for the treatment and improvement of heavy metal-contaminated soil.

Organically modified rectorite has a strong adsorption capacity for Cu^{2+}. The maximum sorption capacities calculated from the pseudo-second-order rate equation and Langmuir isotherm total 209.5 and 201.6 mg/g, respectively [7]. The adsorption behavior of Gemini surfactant-modified rectorite could be accurately described by Freundlich adsorption isotherm model, and its maximum adsorption capacity is 15.16 mg/g [8]. The pore channels of natural B could be dredged by acid activation modification, which is conducive to the diffusion of heavy metal ions, whereas the Cu^{2+} removal rate could reach 98.2% [9]. Dong and Lin [10] studied the purification capability of modified mushroom medium waste on copper ions and observed that the adsorption performance of copper ions in aqueous solution considerably improved, and the removal rate exceeded 95% [10]. Given that cationic and anionic modified materials could only remove single pollutants [11,12], the use of amphiphilic modifiers for preparing amphoteric materials could simultaneously adsorb both organic compounds and heavy metals [13–15]. The effect of Cd^{2+} adsorption in Lou soil modified by amphoteric modifier dodecyl betaine (BS-12) is better than that of unmodified Lou soil, and the adsorption capacity is 1.3–1.8 times higher than that of unmodified soil samples [16]. To confirm the role of amphoteric clay in soil remediation, Li et al. [17] added BS-12 modified B to Lou soil and noted that the adsorption capacity of Cr(VI) increased by 1.52–5.12 times, and the adsorption mechanism mainly involved electrostatic attraction. Therefore, the adsorption capacity of heavy metals could be significantly improved by BS-12 modification, which has broad application prospects in the field of soil pollution remediation.

At present, the application of amphoteric modified materials in contaminated soil is mainly based on the adsorption of the same modifier of a single pollutant, the same heavy metal with different charges, or composite pollution of organic matter and heavy metal [18–20]. However, studies rarely reported the comparative study of adsorption properties of different adsorption materials modified by amphoteric modifiers on heavy metal ions. Nanchong is located in the intersection of the mountainous of northern Sichuan and the hilly areas of central Sichuan. The development of large-scale livestock and poultry farming has caused serious soil contamination with Cu^{2+}. If the widely used B, D, and activated carbon (C) are modified by amphoteric modifiers and added to the typical Cu^{2+} contaminated purple soil (P) in Nanchong, the adsorption capacity of Cu^{2+} by P could be enhanced. The effects of adding different amphoteric materials have also been compared, thus providing a strong regional application value. However, the related studies are limited.

To compare the effects of adding different amphoteric modified materials on the adsorption of Cu^{2+} by typical P, we used 100%BS-12 (as measured by the cation exchange capacity [CEC] of the material) as an amphoteric modifier and modified B, D, C, M, and active calcium silicate (S) to obtain five kinds of modified materials. Then, the different amphoteric modified materials were added to P with the mass ratios of 1% and 2%. In this paper, the isothermal adsorption and thermodynamic characteristics of Cu^{2+} on different mixed soil samples were studied, and the effects of temperature, pH, and ionic strength on Cu^{2+} adsorption were discussed to provide a theoretical basis for the application of amphoteric modified materials to enhance the adsorption of heavy metal ions in soil.

2. Materials and methods

2.1. Experimental materials

Tested substrate materials: C, M, D, B, and S were used as adsorption materials. Table 1 shows the physicochemical properties of all tested materials.

Tested modifier: BS-12 (AR, Tianjin Xingguang Auxiliary Factory) was used as an amphoteric surface modifier.

Test soil: Purple soil was collected from the test field 100 m southwest of the lamp field of China West Normal University. The surface soil samples (0–25 cm) were collected by the S-spot method in typical area, mixed evenly, dried and ground, and passed through 100 mesh (0.15 mm) nylon sieve for storage. The initial Cu^{2+} content of the soil sample was 18.60 mg/kg, the *total organic carbon* content was 18.27 g/kg, and the clay content was 22.43%. Table 1 lists the physical and chemical properties.

Heavy metal pollutant Cu^{2+} was prepared using $CuSO_4\cdot 5H_2O$ (AR, Chengdu Kelon Chemical).

2.2. Preparation of amphoteric modified materials

A wet process was used to prepare amphoteric modified materials [14]. In this process, 100 g raw materials (B, D, C, M, and S) were slowly added to 1.0 L dH_2O, and a certain ratio (100%) of BS-12, which was calculated on the basis of the CEC of raw materials, was added. After stirring at 40°C for 3 h, the samples were separated. The amphoteric modified materials were washed thrice by deionized water, dried at 60°C for 12 h, and passed through a 60 mesh sieve. Next, BS-12 modified B (B_{100BS}), BS-12 modified D (D_{100BS}), BS-12 modified C (C_{100BS}), BS-12 modified M (M_{100BS}), and BS-12 modified S (S_{100BS}) were prepared. Table 2 shows the physicochemical properties of different amphoteric modified materials.

The weight of BS-12 for a certain weight of raw materials can be obtained by using Eq. (1):

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

where W is the mass of the modifier in g, m is the mass of the material in g, CEC is the cationic exchange capacity of the modified material in mmol/kg, M is the molar weight of the modifier in g/mol, R is the modified proportion of the modifier, and b is the content (mass fraction) of the modifier product.

2.3. Experimental design

In the following experimental design, three replicates were set for each treatment.

Table 1
Physical and chemical properties of P and tested materials

Tested samples	Producing area	pH	CEC (mmol/kg)	Specific surface area (m^2/g)
P	Nanchong, Sichuan	8.13	273.22	97.11
B	Xinyang, Henan	10.21	1,001.25	62.88
D	Chifeng, Neimenggu	7.20	330.12	67.26
C	Liyang, Jiangsu	9.15	176.20	1,368.33
M	Qiqihaer, Heilongjiang	8.60	180.24	5.02
S	Lingshou, Hebei	9.93	445.36	114.24

Table 2
Physicochemical properties of amphoteric modified materials

Amphoteric modified materials	pH	CEC (mmol/kg)	Specific surface area (m^2/g)
B_{100BS}	8.34	569.70	6.25
D_{100BS}	6.97	127.68	5.64
C_{100BS}	7.25	78.20	96.57
M_{100BS}	7.08	72.35	2.11
S_{100BS}	8.06	95.53	16.26

2.3.1. Effect of Cu^{2+}adsorption by P

B_{100BS}, D_{100BS}, C_{100BS}, M_{100BS}, and S_{100BS} were added to P at the ratios of 1% and 2% (mass ratio). Ten mixed soil samples, including 1%B_{100BS}, 1%D_{100BS}, 1%C_{100BS}, 1%M_{100BS}, 1%S_{100BS}, 2%B_{100BS}, 2%D_{100BS}, 2%C_{100BS}, 2%M_{100BS}, and 2%S_{100BS}, were obtained after fully stirring and mixing. Isothermal adsorption experiments of Cu^{2+} were carried out with P as the control.

The concentrations of Cu^{2+} were set at nine concentration gradients of 0, 20, 40, 80, 120, 200, 300, 400, and 500 mg/L. The experimental temperature was controlled at 30°C, the pH was 4, and the ionic strength was 0.1 mol/L NaCl.

2.3.2. Effect of environmental factors on Cu^{2+}adsorption

The main environmental factors were temperature, pH value, and ionic strength.

The experimental temperatures were set to 20°C, 30°C, and 40°C (pH value of the initial solution: 4; ionic strength: 0.1 mol/L NaCl). The pH of the initial solution was set to 3, 4, and 5 (initial solution temperature: 30°C; ionic strength: 0.1 mol/L NaCl). The ionic strength of the initial solution was set to 0.01, 0.1, and 0.5 mol/L NaCl (initial solution temperature: 30°C; pH: 4).

2.4. Experimental methods

Batch equilibrium method was used for Cu^{2+} adsorption. A total of 0.1000 g samples were weighed in nine 50 mL plastic centrifuge tubes, and 20.00 mL Cu^{2+} solution with different concentration gradients was added into the pipette under the conditions of at a constant temperature of 30°C, 150 rpm, and 12 h oscillation (the preliminary kinetic experiments showed that adsorption equilibrium was reached after 12 h) [8]. The equilibrium adsorption of Cu^{2+} in the supernatant was determined by centrifugation at 4,800 rpm for 20 min, the equilibrium adsorption amount of Cu^{2+} was determined, and the equilibrium adsorption amount of each material was calculated by subtraction. The Cu^{2+} content was determined via flame atomic absorption spectrophotometry, and background absorption was corrected through the Zeeman effect.

2.5. Data treating

The equilibrium adsorption amount of Cu^{2+} for each mixed soil sample was calculated in accordance with Eq. (2):

$$q = \frac{\left(c_0 - c_e\right)V}{m} \tag{2}$$

where c_0 (mmol/L) and c_e (mmol/L) are the initial and equilibrium concentrations of Cu^{2+} in the solution, respectively. V (mL) is the volume of Cu^{2+} solution added. m (g) is the weight of the tested material. q (mmol/kg) is the equilibrium adsorption amount of Cu^{2+} on the tested material.

The adsorption isotherms were fitted with the Langmuir [21] and Freundlich [19] isotherm models, which are respectively expressed in Eqs. (3) and (4):

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

$$q = kc^{(1/n)} \tag{4}$$

where q is the equilibrium adsorption amount (mmol/kg), q_m is the maximum adsorption amount of Cu^{2+} on the soil sample (mmol/kg), b is the apparent equilibrium constant of the adsorption of Cu^{2+} on the soil sample and can be measured the affinity of the adsorption, c is the equilibrium concentration of Cu^{2+} in the solution (mmol/L), k is a parameter related to the adsorption capacity, and n is the affinity.

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 parametes; Eqs. (5)–(7) are as follows:

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

$$\Delta H = R\left(\frac{T_1 \cdot T_2}{T_2 \cdot T_1}\right) \cdot \ln\left(\frac{K_a, T_2}{K_a, T_1}\right) \tag{6}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{7}$$

where ΔG° is the standard free energy change (kJ/mol), R is a constant (8.3145 J/mol K), T is the adsorption temperature ($T_1 = 293.16$ K, $T_2 = 313.6$ 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. Effects of different amphoteric materials on Cu^{2+} adsorption by P

As shown in Figs. 1a–d, the adsorption isotherms of Cu^{2+} on the mixed soil samples exhibited an "L" shape, and the adsorption capacity of Cu^{2+} increased with the increase in equilibrium concentration. Under the same equilibrium concentration, the adsorption capacity of Cu^{2+} was strengthened when 2% amphoteric materials were added. Langmuir and Freundlich models were used to fit the adsorption isotherm of Cu^{2+} on each soil sample (Table 3). The fitting correlation coefficients reached a highly significant correlation level ($p < 0.01$), indicating that the adsorption of Cu^{2+} by each mixed soil sample followed the Langmuir and Freundlich isotherm adsorption models.

In Table 3, the maximum adsorption capacity (q_m) of Cu^{2+} on all tested soil samples was between 89.12 and 137.16 mmol/kg, which was 1.08–1.42 (1% addition ratio) and 1.19–1.54 times (2% addition) the adsorption capacity of P, respectively. In addition, the trend of $B_{100BS} > D_{100BS} > C_{100BS} > S_{100BS} > M_{100BS} > P$ was showed under the two addition ratios, showing agreement with the adsorption isotherm results. The adsorption constant b of Cu^{2+} on each mixed soil sample was larger than that of P, indicating that the

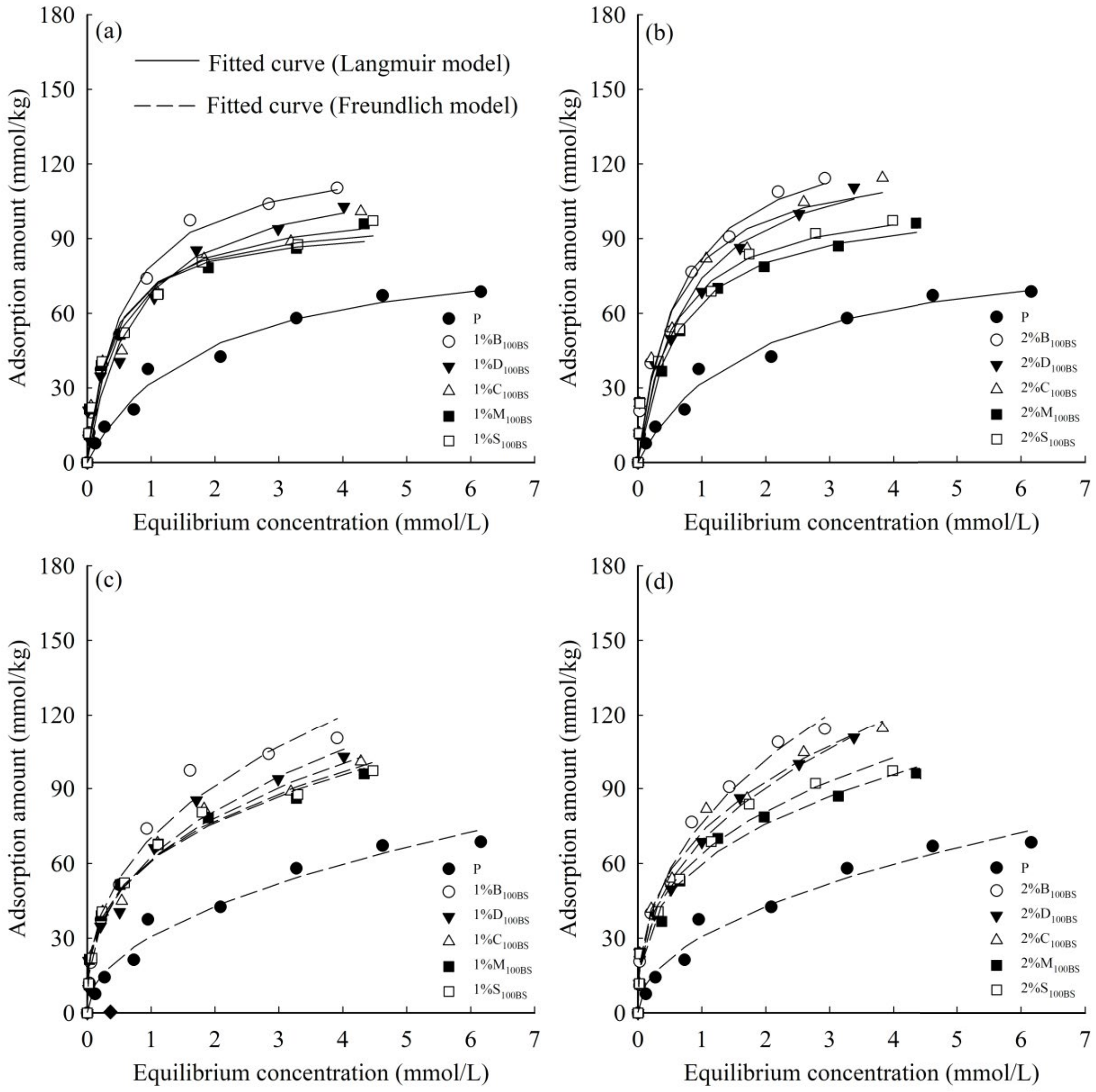

Fig. 1. (a–d) Adsorption isotherms of Cu^{2+} on different tested soil samples.

Table 3
Fitting parameters of Cu^{2+} adsorption on different samples by Langmuir and Freundlich model

Tested soil samples	Langmuir			Freundlich		
	Correlation coefficients/r	q_m (mmol/kg)	b (L/mmol)	Correlation coefficients/r	k	n
P	0.9895**	89.12	0.56	0.9858**	30.68	2.08
1%B_{100BS}	0.9925**	126.19	1.71	0.9881**	70.37	2.62
1%D_{100BS}	0.9770**	119.09	1.34	0.9902**	62.81	2.66
1%C_{100BS}	0.9821**	105.48	1.95	0.9934**	61.46	2.84
1%M_{100BS}	0.9844**	96.34	2.73	0.9927**	61.11	3.10
1%S_{100BS}	0.9884**	99.31	2.46	0.9932**	61.49	3.05
2%B_{100BS}	0.9850**	137.16	1.54	0.9950**	76.50	2.43
2%D_{100BS}	0.9762**	129.46	1.35	0.9959**	69.24	2.56
2%C_{100BS}	0.9776**	123.98	1.83	0.9943**	72.63	2.79
2%M_{100BS}	0.9743**	106.33	1.57	0.9909**	60.07	2.97
2%S_{100BS}	0.9779**	109.17	1.77	0.9933**	64.08	2.95

**indicates that there is a significant correlation at the level of $p = 0.01$, and at the degrees of freedom of $f = 8$ and $p = 0.01$, and $r = 0.765$.

adsorption intensity of Cu^{2+} on P increased after the addition of amphoteric modified materials. The k parameter (related to the adsorption capacity in Table 3) was between 30.68 and 70.50, indicating the same rank in different soil samples as that of q_m. The adsorption intensities n of different tested samples were all greater than 1, indicating that the tested samples have a strong adsorption affinity for Cu^{2+}, and the adsorption is saturated.

The above results were due to the high CEC or specific surface area of the materials. The larger the CEC was, the more the cation sites that could be exchanged on the material surface, producing more Cu^{2+} that could be exchanged with the material; this result supports the findings of Li et al. [22]. Based on the analysis of the correlation between CEC (amphoteric modified materials) and q_m and k, the values of q_m and k increased with the increase in CEC, indicating that the CEC of materials is the key factor that determines Cu^{2+} adsorption by different mixed soil samples.

Pseudo-first-order and pseudo-second-order kinetic models were used to simulate the time-varying data (1% addition ratio) of Cu^{2+} adsorption. Table 4 shows the parameter results of the kinetic models. Results show that the fitting correlation by the pseudo-first-order kinetic was better than that of pseudo-second-order, and all R^2 values were above 0.99. The q_e value obtained from the equation was consistent with the measured experimental value, indicating that the adsorption of modified materials toward Cu^{2+} conformed with the quasi-first-order kinetic model. Cu^{2+} adsorption was considerably affected by the diffusion of Cu^{2+}, and the adsorption isotherm fitted better the Freundlich model than the Langmuir model, indicating that the heterogeneity of the material surface affected Cu^{2+} adsorption.

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

Fig. 2 shows the effects of different temperature treatments on Cu^{2+}adsorption by different soil samples. At 20°C–40°C, the adsorption amount for Cu^{2+} on all soil samples increased with the rise in temperature, and the increasing trend was evident. Under the two addition ratios, which were increased by 1.22–1.49 (1% addition ratio) and 1.25–1.31 times (2% addition ratio). In this process, chemical adsorption played a dominant role. The adsorption capacity for Cu^{2+} with the addition of amphoteric materials was higher than CK at the same temperature. The increase in temperature could intensify the irregular movement of molecules, which was beneficial to the sufficient contact between Cu^{2+} and the adsorption site, and enhance the adsorption effect. In addition, the increase in temperature could aggravate the movement rate of Cu^{2+} toward the pores of the soil samples, indicating pore adsorption. This process also resulted in the interaction of charge attraction, ion exchange, and surface complexation [22].

3.3. Effect of ionic strength on Cu^{2+} adsorption

Fig. 3 shows that with ionic strength (I) within the range of 0.01–0.5 mol/L, the adsorption capacity of P for Cu^{2+} gradually decreased with the increase in ionic strength, whereas that on the tested soil samples initially increased and then decreased, and reached the highest at $I_{0.1}$ (I = 0.1 mol/L) and the lowest at $I_{0.01}$. The adsorption amount for Cu^{2+} of all mixed soil samples increased by 1.39%–9.73%. The above results were mainly due to the low concentration of electrolytes in low ionic strength and the continuous increase in conductivity of the solution with the increased ionic strength of the solution. At high ionic strength, the electrolyte could enhance the adsorption on the surface of soil samples by compressing the dual electric layer. However, when the ionic strength increased to a certain extent, dual electric layer compression was evident, and the electrostatic gravitational distance decreased [23,24]. Simultaneously, Na^+ occupied a large amount of negative point charge on the soil surface. Hence, the ions adsorbed at the electro-adsorption point were saturated, competing with Cu^{2+} for adsorption. Therefore, the electro-adsorption of Cu^{2+} by the

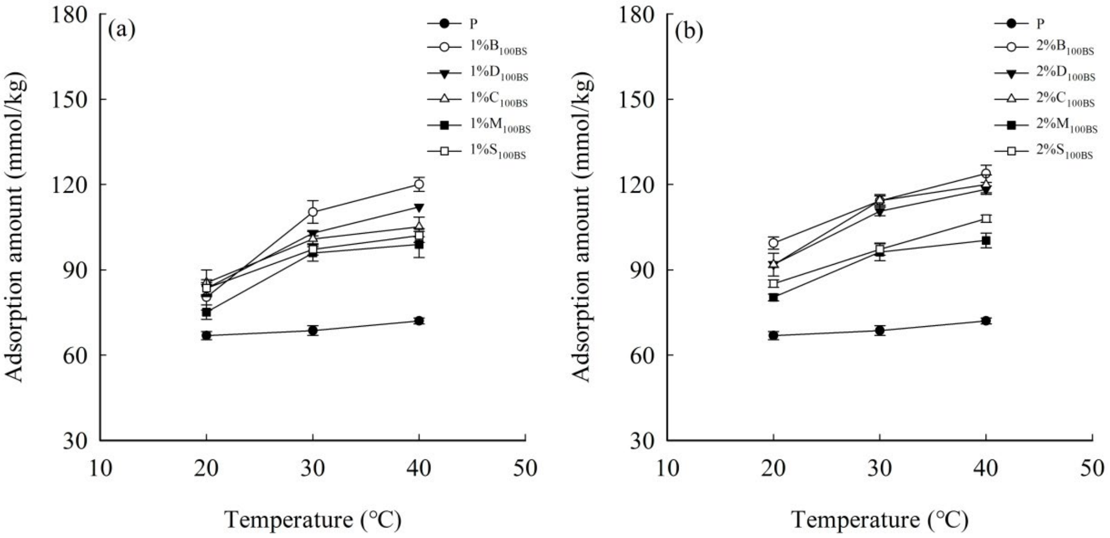

Fig. 2. (a and b) Effect of temperature on Cu^{2+} adsorption by different mixed soil samples.

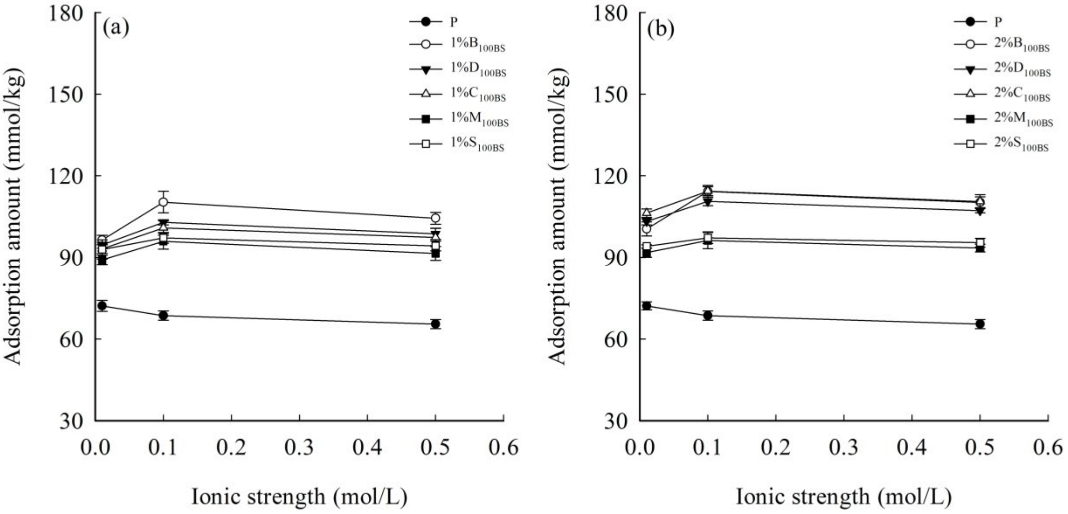

Fig. 3. (a and b) Effect of ionic strengths on Cu^{2+} adsorption on different mixed soil samples.

soil was reduced. 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+} [25,26]. Therefore, the increase in ionic strength was not conducive to the adsorption of Cu^{2+}.

3.4. Effect of pH value on Cu^{2+} adsorption

Fig. 4 shows the effects of different pH on Cu^{2+} adsorption by various soil samples. When the pH changed from 3 to 5, the adsorption capacity for Cu^{2+} of each tested soil sample increased gradually with the increase in pH, showing a positive correlation. The adsorption capacity for Cu^{2+} increased by 8.65%–21.97% with the highest increase in B_{100BS} (21.97%) and the smallest in M_{100BS} (8.65%). The adsorption capacity increased with the increase in addition ratio.

At low pH, the positive charge on the soil surface increased, whereas the negative charge decreased, indicating competitive adsorption between H^+ and Cu^{2+} in the solution, which was unfavorable for the adsorption of Cu^{2+}. As the pH increased, the concentration of OH^- in the equilibrium solution increased, the enhancement of negative charge on the surface of the soil sample, and the partial variable negative charge of BS-12 hydrophilic group both promoted the adsorption of Cu^{2+}, and the competitive adsorption was weakened. High pH is beneficial to the hydrolysis of Cu^{2+}, and the adsorption heat of hydroxyl cation (MOH^+) on the soil surface is low [26]. The adsorption affinity of MOH^+ on the soil is higher than that of free metal ion M^{2+}. Therefore, high pH is favorable to the adsorption of MOH^+ on the soil. With the increase in pH, the number of OH^- ions increased, which easily coprecipitated with Cu^{2+} [27,28] and then deposited on the soil surface for removal.

Table 4
Coefficients of pseudo-first/second-order adsorption kinetic models

Soil samples	pseudo-first-order adsorption kinetic models			pseudo-second-order adsorption kinetic models		
	q_e (mmol/kg)	k_1 (h^{-1})	R^2	q_e (mmol/kg)	k_2 (kg/mmol/h)	R^2
P	68.20	0.7623	0.9944	72.58	0.0149	0.9781
1%B_{100BS}	109.42	0.5079	0.9902	118.07	0.0062	0.9887
1%D_{100BS}	104.07	0.3592	0.9968	114.12	0.0044	0.9792
1%C_{100BS}	101.50	0.3446	0.9954	111.00	0.0045	0.9854
1%M_{100BS}	96.54	0.3437	0.9967	105.82	0.0046	0.9830
1%S_{100BS}	97.70	0.3567	0.9955	106.78	0.0047	0.9828

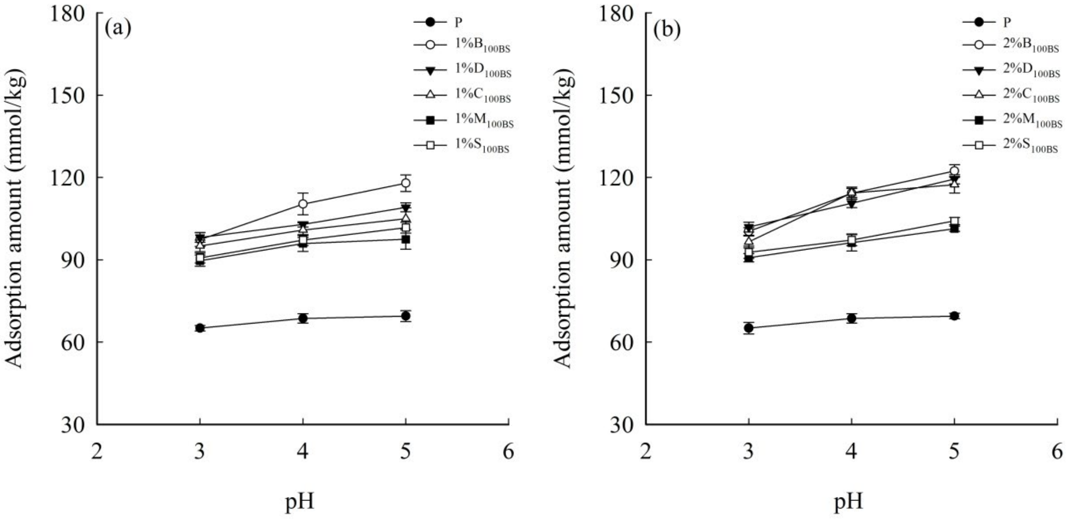

Fig. 4. (a and b) Effect of pH on Cu^{2+} adsorption on different mixed soil samples.

3.5. Thermodynamic characteristics of Cu^{2+} adsorption on mixed soil samples

Based on the thermodynamic parameters of Cu^{2+} adsorption on each tested soil sample in Table 5, the free energy of Cu^{2+} adsorption on each soil sample was negative at 20°C and 40°C, indicating that Cu^{2+} adsorption on soil samples is a spontaneous process. Under the same conditions, $|\Delta G_{40}| > |\Delta G_{20}|$ were presented, indicating that high-temperature results in strong spontaneity, consistent with the results of endothermic reactions mentioned above. In terms of enthalpy and entropy, Cu^{2+} adsorption on each soil sample had $\Delta H > 0$ and $\Delta S > 0$, indicating that the adsorption of Cu^{2+} by soil samples was endothermic and entropy increasing. This condition was mainly due to the ion exchange (endothermic) reaction of the amphoteric modified materials to Cu^{2+} and the low degree of confusion in the adsorption process. The adsorption mechanism was mainly affected by the mechanism of amphoteric modified materials.

The molecular structure of BS-12 is a dodecyl hydrophobic carbon chain that contains a positively charged quaternary amine group and negatively charged carboxyl hydrophilic group. After modification of B, D, C, M, and S by BS-12, the positive charge at the hydrophilic end of BS-12 reacted with the negative charge on the surface of the material, causing the negative charge at the hydrophilic end and the hydrophobic carbon chain to extend outward [29,30]. Subsequently, the complexation of Cu^{2+} by the material was remarkably enhanced. With the increase in BS-12 modification on the material surface, the BS-12 entered the interlayer of the material and occupied the interlayer position irreversibly, thus weakening the adsorption capability for Cu^{2+}. When the modification ratio of B reaches 100%, the adsorption capacity of Cu^{2+} increases [31]; ideal results could be achieved by modifying all materials with 100% BS-12. Through the mutual attraction of the hydrophobic bond of the amphoteric modifier, the adjacent clay sheets in the soil sample aggregated to form a large agglomerate; thereafter, the amphoteric modifier could be gradually transferred from the outer surface of the cosmid to the inner surface or interlayer of the clay mineral [32]. The inorganic cations placed on the outer surface of the agglomerate could undergo ion exchange and adsorption on the surface of the amphoteric modified soil sample. In summary, the adsorption of Cu^{2+} by each mixed soil sample involved chemical adsorption, supplemented by complexing adsorption and ion exchange as the main mechanism of Cu^{2+} adsorption.

Table 5
Thermodynamic parameters of Cu^{2+} adsorption on different tested soil samples

Tested soil samples	ΔG_{20} (kJ/mol)	ΔG_{40} (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol/K)
P	–15.37	–16.62	2.84	0.06
$1\%B_{100BS}$	–17.37	–19.60	15.31	0.11
$1\%D_{100BS}$	–17.04	–18.97	11.30	0.10
$1\%C_{100BS}$	–18.06	–19.83	7.90	0.09
$1\%M_{100BS}$	–18.69	–20.68	10.51	0.10
$1\%S_{100BS}$	–18.66	–20.45	7.62	0.09
$2\%B_{100BS}$	–17.55	–19.32	8.37	0.09
$2\%D_{100BS}$	–17.11	–18.94	9.65	0.09
$2\%C_{100BS}$	–17.77	–19.68	10.19	0.10
$2\%M_{100BS}$	–17.49	–19.27	8.49	0.09
$2\%S_{100BS}$	–17.90	–19.74	9.07	0.09

4. Conclusion

The maximum adsorption amount of Cu^{2+} for each tested soil sample ranged from 89.12 mmol/kg to 137.16 mmol/kg, following the trend $B_{100BS} > D_{100BS} > C_{100BS} > S_{100BS} > M_{100BS} > P$. The adsorption amount at 2% addition ratio was slightly higher than that at 1%. At 20°C–40°C, Cu^{2+} adsorption on the soil samples showed a positive temperature effect. With the increase in ionic strength, the adsorption amount of Cu^{2+} on each soil sample increased first and then decreased, and the peak value was observed at $I_{0.1}$ (I = 0.1 mol/L). The increasing pH was beneficial to the adsorption of Cu^{2+} by different mixed soil samples. The adsorption of Cu^{2+} by mixed soil samples was a spontaneous, endothermic, and entropy increasing process.

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