



## Adsorption characteristics of Cu<sup>2+</sup> by amphoteric and nanometer zero-valent iron modified bank soil from Jialing River (Sichuan section)

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Received 28 September 2020; Accepted 22 February 2021

### ABSTRACT

To study the adsorption characteristics of Cu<sup>2+</sup> by amphoteric and nanometer zero-valent iron (NZVI)-modified riverbank soil, we used dodecyl dimethyl betaine (BS-12) for amphoteric modification of bank soils from the Jialing River (Sichuan section). Then, NZVI was loaded on the BS-12-modified riverbank soils by liquid-phase reduction. The physicochemical characteristics of different BS-12-and BS-NZVI (BS-12 and NZVI)-modified riverbank soils and their adsorption differences were studied under various conditions (pH, ion strength, and temperature). In addition, the isothermic adsorption and thermodynamic characteristics of Cu<sup>2+</sup> on BS-12-and BS-NZVI-modified riverbank soils were analyzed. Results showed the following: (1) pH, cation exchange capacity and specific surface area ( $S_{\text{BET}}$ ) of different BS-12-and BS-NZVI-modified soils decreased, whereas their total organic carbon (TOC) increased. The surface of the original soils became smooth after BS-12 modification, whereas the surface of BS-12-modified soils became rough after loading with NZVI. NZVI was evenly distributed on the BS-NZVI-modified soil surface. (2) pH had minimal effect on the adsorption of Cu<sup>2+</sup> by different soil samples. The adsorption of Cu<sup>2+</sup> by different modified soils was promoted first and then restrained with the increase in ion strength. In the range of 20°C–40°C, the adsorption amount of Cu<sup>2+</sup> by different modified soils showed a positive temperature effect. (3) The adsorption isotherms of Cu<sup>2+</sup> for BS-12-and BS-NZVI-modified soils were all L-shaped, and the adsorption amount of Cu<sup>2+</sup> by different soil samples was ranked in the order of BS-NZVI modification > BS-12 modification > without modification. BS-NZVI-modified soil samples effectively improved the removal rate of Cu<sup>2+</sup>. The adsorption of Cu<sup>2+</sup> by different soil samples was a spontaneous, endothermic, and entropy-adding process. (4) TOC and  $S_{\text{BET}}$  were the key factors that determined the maximum adsorption amount of Cu<sup>2+</sup> by BS-12-and BS-NZVI-modified riverbank soils.

**Keywords:** Dodecyl dimethyl betaine; Nanometer zero-valent iron; Riverbank soil; Cu<sup>2+</sup>; Adsorption amount

### 1. Introduction

Different kinds of pollutants have been deposited in bank soil due to the long-term discharge of waste from urban industrial and agricultural production along rivers

[1]; among these pollutants, heavy metals cause serious pollution [2,3]. With the continuous runoff and migration, pollutants would eventually enter the river, resulting in different degrees of pollution to river water [4] and posing a potential threat to river ecological security and the health

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of residents [5]. Therefore, studies should focus on how to prevent and control the migration and transformation of pollutants to the riverbank soil for protecting river ecological environment and human health.

Riverbank soil is the last barrier to prevent pollutants from entering the river water directly, but its low clay content results in the easy migration of pollutants, which are produced by industrial and agricultural production, into the river. Chemical modification can improve the adsorption and fixation capability of riverbank soil toward pollutants. Scholars have used cationic, double cationic, and anionic modifiers to modify different kinds of clay, and the results showed that the modified clay has a stronger adsorption capacity for organic pollutants than unmodified clay [6,7]. Meanwhile, cationic modifiers are expensive and bactericidal; thus, they are not the best choice for soil modification [8]. The clay modified by cationic surfactants can improve the adsorption of organic pollutants, but their adsorption capability for heavy metal cations is reduced, and the effect of simultaneous and efficient treatment of organic and heavy metal pollution cannot be achieved [9]. Amphoteric modifiers have positively and negatively charged hydrophilic groups and hydrophobic carbon chains, which can effectively enhance the adsorption capacity of clay to heavy metal ions and organic pollutants [10,11]. The amphoteric modified clay can simultaneously adsorb  $\text{Cd}^{2+}$  and phenol (or bisphenol A), but the simultaneous adsorption effect is slightly poor [12,13]. In the study of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  adsorption by the amphoteric modified bentonite, the studied material was more beneficial to the adsorption of  $\text{Cu}^{2+}$  than  $\text{Pb}^{2+}$  [14].

Nanoscale zero-valent iron (NZVI) has been widely used in ecological environment protection and pollution control because of its strong reducibility, large specific surface area, high surface activity, and good adsorption performance [15,16]. NZVI can efficiently remove heavy metals and organic pollutants from water; it has become a research focus in the field of environmental remediation observed that NZVI could remove more than 97% of  $\text{Pb}^{2+}$  from the water after 1 h of reaction [17–19]. A total of 0.01 g NZVI could completely reduce Cr(VI) in 1 g tannery waste in 2 h, and the process accords with the quasi-first-order kinetics [20]. Cao and Zhang [21] showed that 1 g NZVI could reduce 84.4–109.3 and 69.3–72.2 mg Cr(VI) in groundwater and chromium-ore processing residue, respectively. However, NZVI presents various problems, such as easy agglomeration and oxidation, a short aging period, and low utilization efficiency [22,23], which limit its application range. To prevent the agglomeration and oxidation of NZVI particles and improve the dispersion and stability between particles, scholars studied the modification of NZVI. The results showed the substantially improved removal efficiency of pollutants by modified NZVI. The optimum removal rate of  $\text{Cd}^{2+}$  by sulfide-modified NZVI was 85 mg/g, which was more than 100% higher than that of the original NZVI [24]. Carboxymethyl cellulose–NZVI has an excellent fixation effect on  $\text{Cu}^{2+}$  in high-sulfur soil [25], and the removal of  $\text{Cu}^{2+}$  from landfill leachate by a starch–NZVI can reach 56.27 mg/g [26].

The typical riverbank  $\text{Cu}^{2+}$  pollution in the Northeast Sichuan Province is caused by the development of the

aquaculture industry. In order to prevent pollutants from entering the river water directly, the retention capacity of riverbank soil to pollutants should be further improved. If the riverbank soil is simultaneously modified by amphoteric modifier and NZVI, the agglomeration of NZVI can be markedly reduced, and the removal efficiency of  $\text{Cu}^{2+}$  can be improved at the same time. However, no current study reports about this topic. In this study, different riverbank soils in the Jialing River (Sichuan section) were used as the research objects, and they were modified by amphoteric modifier dodecyl dimethyl betaine (BS-12) and NZVI. The physicochemical characteristics of different modified riverbank soils and their adsorption differences were studied under varied pH, ion strength, and temperature conditions. In addition, the isothermic adsorption and thermodynamic characteristics of  $\text{Cu}^{2+}$  on modified riverbank soils were analyzed to provide a reference scheme for the protection of water resources in the Northeast Sichuan aquaculture area.

## 2. Materials and methods

### 2.1. Materials

Analytical reagent (AR)-grade  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NaBH}_4$ , and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  were purchased from ChengDu Kelon Chemical Reagent Factory, ChengDu City, Sichuan Province, China. AR-grade BS-12 in water [30% (w/v)], which was provided by Xingguang Auxiliary Factory (Tianjin City, China), was used as the amphoteric modifier [27].

Bank soil samples were collected from the Sichuan section of the Jialing River, and the sampling points from north to south were Nanbu (NB), Cangxi (CX), and Jialing (JL). Within 50 m from the riverbank, a typical area (with the same vegetation type and land use pattern) was selected, and 0–20 cm soil samples were collected by multi-point sampling. The soil samples were mixed evenly, air-dried and then passed through a 60-mesh sieve.

### 2.2. Preparation of modified riverbank soils

BS-12-modified riverbank soil samples were prepared by the wet method [28]. In this process, 100 g bank soil was slowly added to 1.0 L distilled water ( $\text{dH}_2\text{O}$ ), followed by the addition of 100% modified BS-12, which was calculated in accordance with the cation exchange capacity (CEC) of bank soils. After stirring at 40°C for 6 h, the samples were centrifuged at 4,800 rpm for 10 min. Then, the supernatant was discarded, and the samples were washed thrice with  $\text{dH}_2\text{O}$  by centrifugation. Different BS-12-modified bank soils (CX, NB, and JL) were obtained after drying at 60°C for 12 h, passed through a 60-mesh sieve, and recorded as  $\text{CX}_{\text{BS}}$ ,  $\text{NB}_{\text{BS}}$ , and  $\text{JL}_{\text{BS}}$  respectively.

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

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

where  $W$  (g) refers to the weight of BS-12,  $m$  (g) refers to the weight of riverbank soil that will be modified, CEC (mmol/kg) represents the CEC of bank soil,  $M$  (g/mol) is

the molecular mass of BS-12,  $R$  stands for the modified proportion of BS-12, and  $b$  specifies the product content of BS-12 (mass fraction).

BS-NZVI-modified riverbank soil samples were prepared by liquid-phase reduction. A total of 5.6 g BS-12-modified soil ( $CX_{BS}$ ,  $NB_{BS}$ , and  $JL_{BS}$ ) was added to 250 mL 0.1 mol/L  $FeSO_4 \cdot 7H_2O$  ethanol- $dH_2O$  mixture (alcohol to water volume ratio was 4:1) and stirred for 1 h to complete mixing. Under the protection of  $N_2$ , 250 mL 0.5 mol/L  $NaBH_4$  aqueous solution was added dropwise and stirred for 2 h. After the reaction was completed, the product was separated by filtration, washed thrice with anhydrous ethanol, and dried in a vacuum at 60°C for 12 h. Then, the samples were passed through a 60-mesh sieve. The samples were recorded as  $CX_{BS-NZVI}$ ,  $NB_{BS-NZVI}$ , and  $JL_{BS-NZVI}$ .

### 2.3. Experimental design

$CX$ ,  $NB$ , and  $JL$  (as control);  $CX_{BS}$ ,  $NB_{BS}$ , and  $JL_{BS}$ ;  $CX_{BS-NZVI}$ ,  $NB_{BS-NZVI}$ , and  $JL_{BS-NZVI}$  (nine samples in total) were measured for pH, CEC, specific surface area ( $S_{BET}$ ), and total organic carbon (TOC) and analyzed by scanning electron microscopy (SEM).

pH, ionic strength, and temperature were considered the environmental factors in the experimental design. The pH of the initial solution was set to 3, 4, and 5. The ionic strength of the initial solution was set to 0.01, 0.1, and 0.5 mol/L (at which the pH was best controlled). The experimental temperatures were set to 20°C, 30°C, and 40°C (at which the best pH and ionic strength were controlled).

The preliminary experiment showed that the adsorption isotherm changed when the concentration reached 300–400 mg/L. Therefore, the concentration gradients of  $Cu^{2+}$  were set at 0, 20, 50, 100, 150, 200, 300, 400, and 500 mg/L. Each treatment was repeated thrice under the best environmental factors (obtained by the experiment for environmental influence).

### 2.4. Experimental methods

pH was determined by a pH meter (Hach HQ411D, USA). The sodium acetate–ammonium acetate method was used to determine the CEC of the samples.  $S_{BET}$  was determined by the Brunauer–Emmett–Teller method (Analyzer ASAP 2400, Micromeritics, USA). TOC was measured by TOC-VCPH (Japan) instrument. Hitachi S-4800 (Japan) scanning electron microscope was used to analyze the sample morphology.

The batch equilibrium method was used for  $Cu^{2+}$  adsorption. A total of 0.20 g tested samples were weighed in nine 50 mL plastic centrifuge tubes, and 20.00 mL  $Cu^{2+}$  solution with different concentration gradients was added to the pipette at a constant temperature of 40°C, 150 rpm, and 12 h oscillation (preliminary kinetic experiments by Deng et al. [29] showed that adsorption equilibrium was reached after 12 h). 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 that of each sample was calculated by subtraction.  $Cu^{2+}$  content was determined via flame atomic absorption spectrophotometry, and background absorption was corrected through the Zeeman Effect.

### 2.5. Data processing

The equilibrium adsorption capacity was calculated using the following formula:

$$q = \frac{(C_0 - C_e)V}{m} \quad (2)$$

In the formula,  $C_0$  (mmol/L) and  $C_e$  (mmol/L) are the initial concentration and equilibrium concentration of  $Cu^{2+}$  in the solution (mmol/L);  $V$  (mL) represents the volume of  $Cu^{2+}$  solution added;  $m$  (g) is the weight of the tested soil samples;  $q$  specifies the equilibrium adsorption capacity of  $Cu^{2+}$  (mmol/kg) on the tested soil.

Based on the adsorption isotherm trend, Langmuir isotherm was selected to fit the  $Cu^{2+}$  adsorption isotherm. Eq. (3) is expressed as follows:

$$q = \frac{q_m bc}{1 + bc} \quad (3)$$

where  $q$  (mmol/kg) is the equilibrium adsorption capacity of  $Cu^{2+}$  for the tested sample;  $c$  (mmol/kg) is the equilibrium concentration of  $Cu^{2+}$  in the solution;  $q_m$  (mmol/kg) refers to the maximum adsorption capacity of the tested sample for  $Cu^{2+}$ ;  $b$  is the adsorption surface equilibrium constant of the tested sample for  $Cu^{2+}$ , and it can be used to measure the affinity of adsorption.

Parameter  $b$  in the Langmuir model is equivalent to the apparent adsorption constant of the equilibrium constant, and the thermodynamic parameter calculated by  $b$  is called the apparent thermodynamic parameter. Eqs. (4)–(6) are as follows:

$$\Delta G = -RT \ln b \quad (4)$$

$$\ln \frac{bT_2}{bT_1} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

where  $\Delta G$  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), and  $\Delta H$  is the enthalpy of adsorption process (kJ/mol), and  $\Delta S$  is the entropy change of adsorption process (J/mol/K).

SPSS 16.0 statistical analysis software was used to process the experimental data for variance and correlation analysis. CurveExpert 1.4 fitting software was used in isothermal fitting, and SigmaPlot 10.0 software was adopted to improve data plotting. The data were expressed as the means with standard deviation, and different letters indicate significant differences among various amendments. Analysis of variance was performed to determine the effects of amendments, followed by Tukey's honestly significant difference test.

## 3. Results and discussion

### 3.1. Surface characteristics of each test sample

Table 1 shows the basic physicochemical characteristics of each test soil sample. The TOC content of the modified

soil samples was notably higher than that of the unmodified ones. However, the pH, CEC, and  $S_{BET}$  of the modified soil samples were reduced compared with those of the unmodified soil samples. After being covered by BS-12 and NZVI of the soil layer surface, the average particle size of the soil samples increased, resulting in a remarkable reduction of  $S_{BET}$ . The SEM of each tested sample (Fig. 1)

showed that unmodified riverbank soils had a compact crystal structure, the surface structure was flat, and the end surface showed no curling phenomenon. The surface structure of BS-12-modified riverbank soils was smoother than that of original soils. After loading NZVI, the tightness of BS-12-modified bank soil surface increased, the surface became rough, and the particle density increased. NZVI was evenly distributed on the BS-NZVI-modified soils with no evident agglomeration.

Table 1  
Basic physicochemical characteristics of tested soil samples

Soil samples	pH values	CEC (mmol/kg)	$S_{BET}$ ( $m^2/g$ )	TOC (mg/kg)
CX	8.16	120.72	90.34	15.75
NB	7.99	118.22	110.44	28.16
JL	7.70	204.08	130.21	12.28
$CX_{BS}$	8.01	89.55	7.27	333.51
$NB_{BS}$	7.55	85.27	11.20	314.26
$JL_{BS}$	7.12	153.78	12.28	366.17
$CX_{BS-NZVI}$	8.12	81.21	15.27	280.27
$NB_{BS-NZVI}$	7.68	77.34	17.62	275.33
$JL_{BS-NZVI}$	7.52	103.28	21.02	268.84

3.2. Effect of pH and ionic strength on  $Cu^{2+}$  adsorption

Fig. 2 shows the effects of pH and ion strength on the adsorption of  $Cu^{2+}$  by different riverbank soils. The adsorption amount of  $Cu^{2+}$  on the tested soils increased in the range of pH 3–5, whereas that of NB,  $CX_{BS}$ ,  $NB_{BS}$ ,  $JL_{BS-NZVI}$  and  $NB_{BS-NZVI}$  at pH = 3 significantly differed from that in pH = 4 and pH = 5. Under acidic conditions, competitive adsorption occurred between  $H^+$  and  $Cu^{2+}$  in the solution, and the competition weakened with the increase in pH. In general, in the range of pH 3–5, pH caused a negligible effect on the adsorption of  $Cu^{2+}$  by each tested soil sample.

When the ionic strength was 0.01–0.5 mol/L, the adsorption amount of  $Cu^{2+}$  on the different soil samples

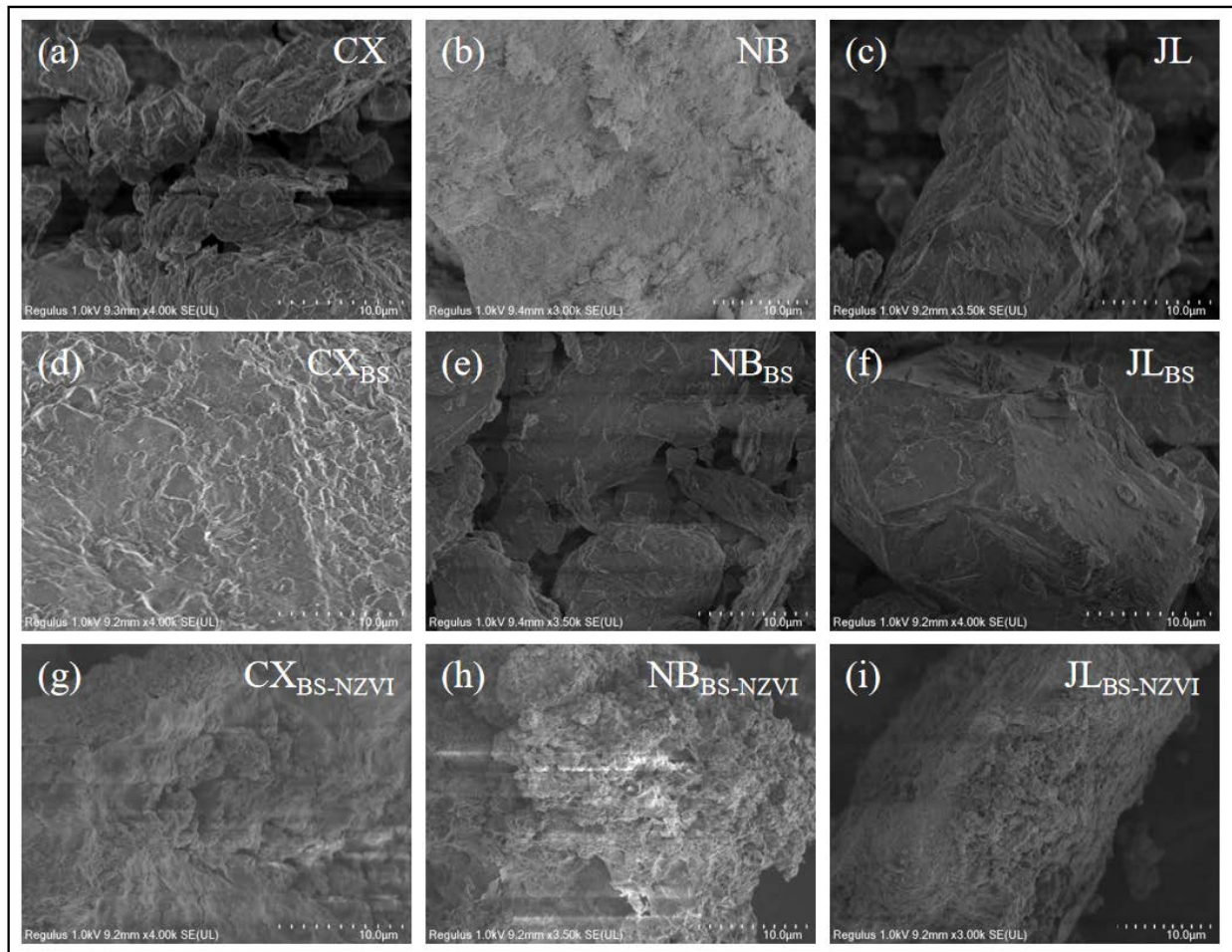


Fig. 1. SEM characteristics of different tested soil samples.

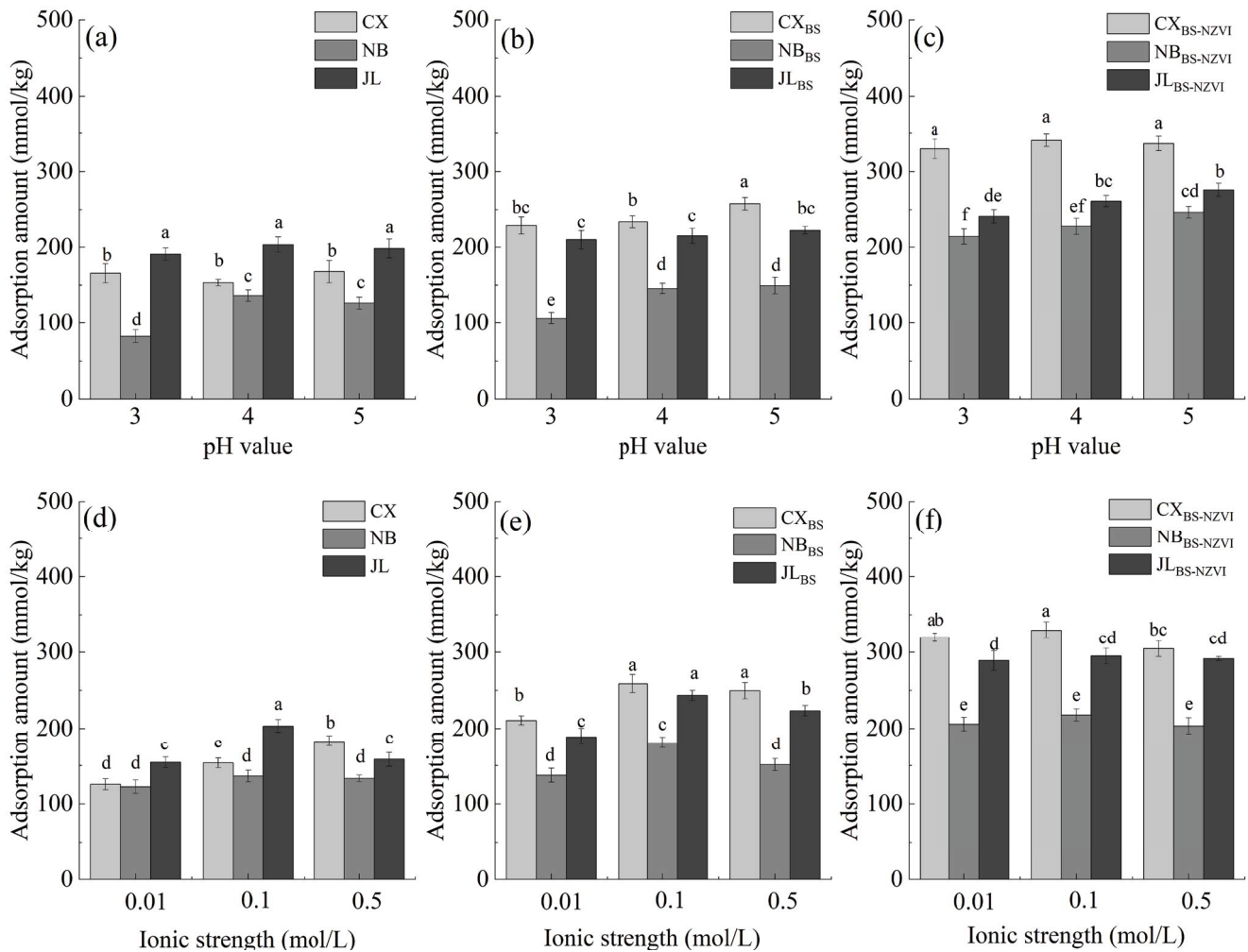


Fig. 2. Effects of pH (a–c) and ionic strength (d–f) on  $\text{Cu}^{2+}$  adsorption.

(except CX) increased at first and then decreased with the increase in ionic strength, showing the largest at the ionic strength of 0.1 mol/L. The adsorption of  $\text{Cu}^{2+}$  on different soil samples was mainly realized by outer complexation or ion exchange. The increase in ionic strength can reduce the activity of  $\text{Cu}^{2+}$  in solutions;  $\text{Na}^+$  and  $\text{Cu}^{2+}$  in background solutions exhibit competitive adsorption on the soil surface [28].

Different lowercase letters indicate a significant difference among pH (ionic strength) treatments at 0.05 levels.

### 3.3. Temperature effect on $\text{Cu}^{2+}$ adsorption

When the temperature increased from 20°C to 40°C (Fig. 3), the adsorption amount of  $\text{Cu}^{2+}$  on each soil sample increased, which indicates a positive temperature effect. The increase in amplitude changed from 8.28% to 57.14% and ranked in the order of  $\text{CX} > \text{CX}_{\text{BS}} > \text{NB} > \text{JL} > \text{JL}_{\text{BS}} > \text{NB}_{\text{BS-NZVI}} > \text{NB}_{\text{BS}} > \text{CX}_{\text{BS-NZVI}} > \text{JL}_{\text{BS-NZVI}}$ . The influence of temperature on  $\text{Cu}^{2+}$  adsorption followed the order: unmodified > BS-modified > BS-NZVI-modified soil. This result was mainly due to the ion exchange effect on  $\text{Cu}^{2+}$  by soil samples and the complexation or chelation of  $\text{Cu}^{2+}$  by BS-12. The chemical reaction exhibited an endothermic reaction

and showed that increased temperature was beneficial to  $\text{Cu}^{2+}$  adsorption [30]. This finding is consistent with the research results on  $\text{Cd}^{2+}$  adsorption by Ren et al. [31].

### 3.4. Isothermal and thermodynamic characteristics of $\text{Cu}^{2+}$ adsorption

Fig. 4 shows the adsorption isotherms and adsorption rates of  $\text{Cu}^{2+}$  for each tested soil sample under the best environmental factors (pH = 5, ionic strength of 0.1 mol/L, and 40°C). The adsorption amount of  $\text{Cu}^{2+}$  increased with the increase in equilibrium concentration, and the adsorption isotherms were all L-type. At the same equilibrium concentration, the adsorption capacity showed the trend of  $\text{CX}_{\text{BS-NZVI}} > \text{NB}_{\text{BS-NZVI}} > \text{JL}_{\text{BS-NZVI}} > \text{JL}_{\text{BS}} > \text{CX}_{\text{BS}} > \text{JL} > \text{NB}_{\text{BS}} > \text{CX} > \text{NB}$ . The maximum adsorption rate ( $R_m$ ) of TC was kept above 72%, and the highest value was 96.84%. The  $R_m$  of BS-NZVI-modified soil was higher than that of unmodified and BS-modified soil.

Table 2 shows the fitting results of the adsorption isotherm via the Langmuir model. The correlation coefficients of the fitting results reached an extremely significant level, indicating that the adsorption of  $\text{Cu}^{2+}$  by different samples

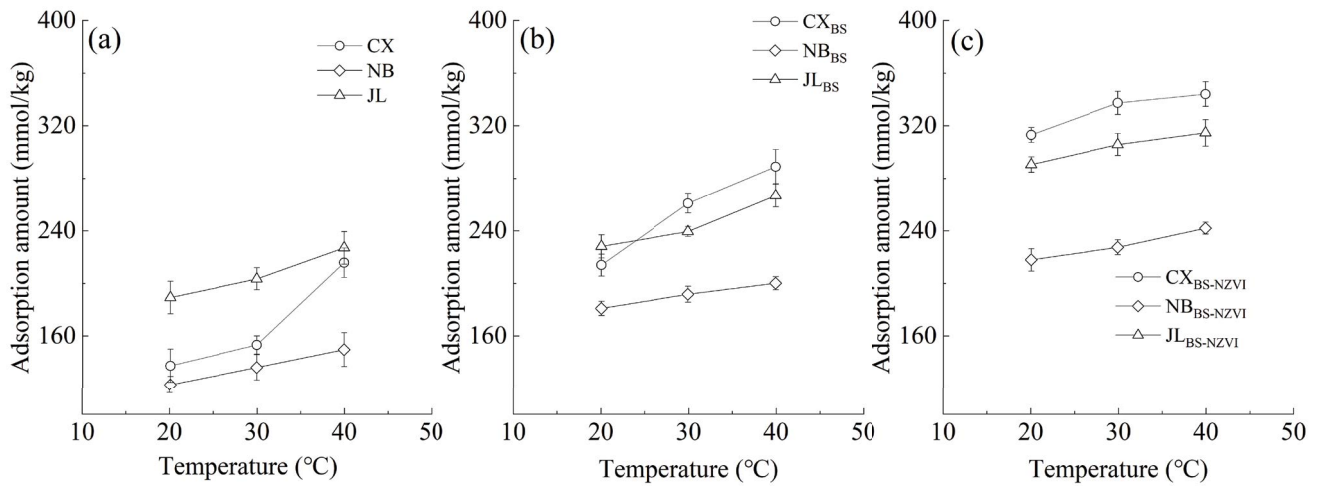


Fig. 3. (a–c) Effect of temperature on Cu<sup>2+</sup> adsorption.

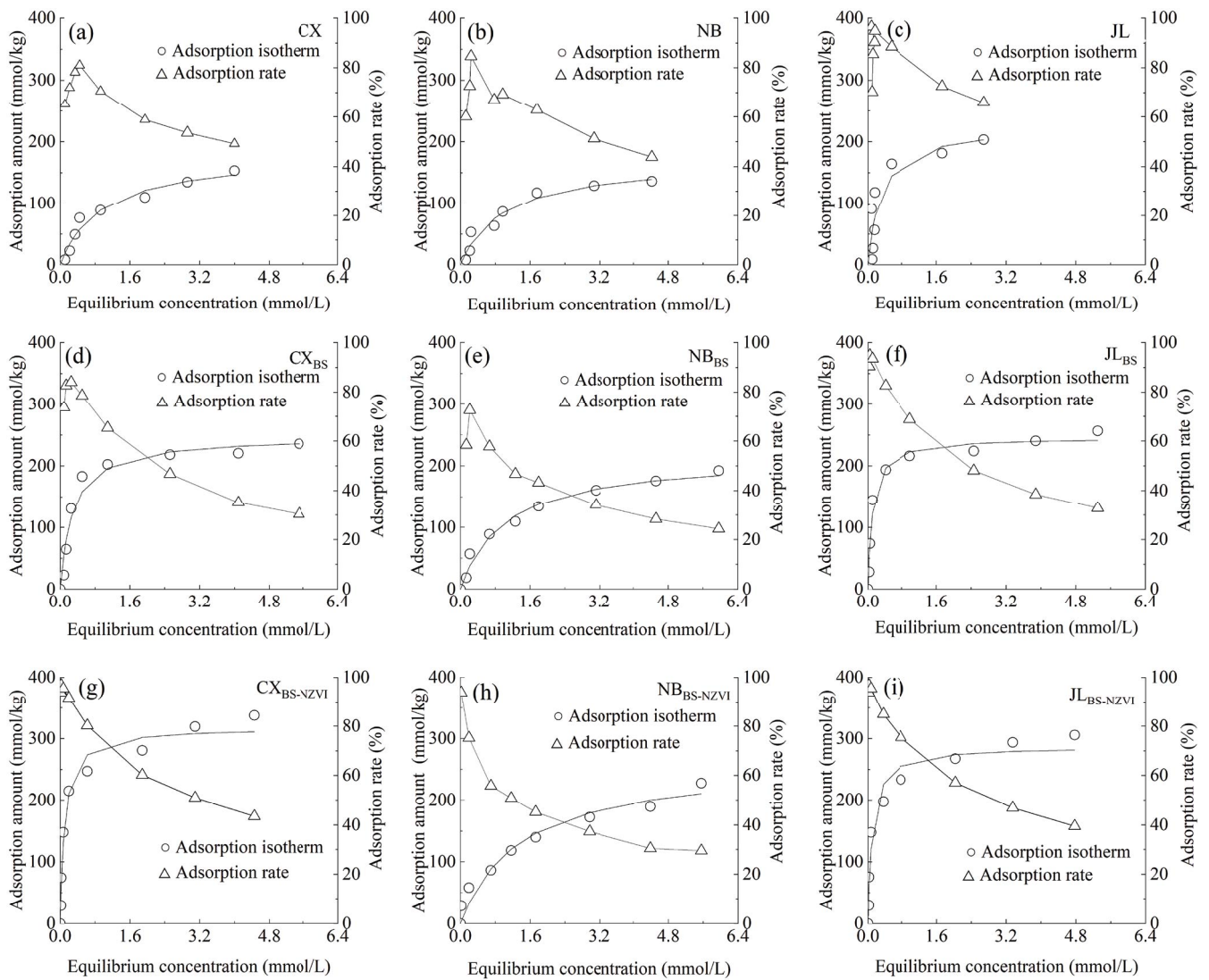


Fig. 4. Isothermal adsorption characteristics of Cu<sup>2+</sup> on tested soil samples.

Table 2  
Langmuir fitting and thermodynamic parameters of Cu<sup>2+</sup> adsorption

Soil samples	Fitting parameters			Thermodynamic parameters			
	Correlations/r	$q_m$ (mmol/kg)	$b$	$\Delta G_{20}$ (kJ/mol)	$\Delta G_{40}$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol/K)
CX	0.9841 <sup>a</sup>	146.47	1.03	-16.64	-18.95	17.25	115.60
NB	0.9814 <sup>a</sup>	139.49	1.00	-16.58	-18.23	7.58	82.43
JL	0.9182 <sup>a</sup>	202.97	3.28	-19.55	-21.36	6.96	90.44
CX <sub>BS</sub>	0.9822 <sup>a</sup>	235.68	3.48	-19.64	-21.76	11.46	106.07
NB <sub>BS</sub>	0.9922 <sup>a</sup>	184.36	0.98	-16.64	-18.04	3.82	69.79
JL <sub>BS</sub>	0.9887 <sup>a</sup>	241.29	9.66	-22.08	-23.99	5.98	95.71
CX <sub>BS-NZVI</sub>	0.9884 <sup>a</sup>	310.96	9.91	-22.24	-24.01	3.61	88.21
NB <sub>BS-NZVI</sub>	0.9811 <sup>a</sup>	210.37	0.73	-15.96	-17.33	4.00	68.09
JL <sub>BS-NZVI</sub>	0.9840 <sup>a</sup>	281.28	10.30	-22.40	-24.13	3.04	86.76

<sup>a</sup>indicates that the correlation coefficient is significant at  $p = 0.01$  level ( $r = 0.765$  when the degree of freedom  $f = 8$  and the level of significance  $p = 0.01$ ).

agreed with the Langmuir model. The maximum adsorption amount ( $q_m$ ) was between 139.49 and 310.96 mmol/kg, and the ranking order was consistent with the adsorption capacity shown in Fig. 4. Compared with the unmodified soil samples, BS-12- and BS-NZVI-modified soil samples exhibited substantial improvement in the adsorption capacity for Cu<sup>2+</sup>. The adsorption amounts of Cu<sup>2+</sup> on BS-12-modified soil samples were 53.87% (CX), 41.18% (NB), and 26.01% (JL) higher than that of unmodified soil samples. Meanwhile, the adsorption amounts of CX<sub>BS-NZVI</sub>, NB<sub>BS-NZVI</sub>, and JL<sub>BS-NZVI</sub> for Cu<sup>2+</sup> were 1.43, 1.18, and 1.19 times higher than that of BS-12-modified soils, respectively. The above results proved that the modification by BS-12 and BS-NZVI increased the Cu<sup>2+</sup> adsorption capacity of the soil samples. The affinity constant  $b$  of each amended soil for Cu<sup>2+</sup> adsorption was maintained in the range of 0.73–10.30, implying an ordinary adsorption affinity.

Table 2 shows the thermodynamic parameters of Cu<sup>2+</sup> adsorption by the different soil samples. At 20°C and 40°C, the apparent free energy changes ( $\Delta G$ ) in Cu<sup>2+</sup> adsorbed by soil samples were less than zero, which indicates that the adsorption was a spontaneous reaction. Under the

same treatment, Cu<sup>2+</sup> adsorption was highly spontaneous at 40°C. The enthalpy change  $\Delta H$  of Cu<sup>2+</sup> was higher than zero, which indicates that the adsorption was an endothermic reaction, and the increase in temperature promoted adsorption. This finding was consistent with the conclusion that the adsorption of Cu<sup>2+</sup> by each soil sample showed a positive temperature effect. The adsorption entropy  $\Delta S$  of each tested soil sample was larger than zero, indicating that the adsorption process was an entropy-adding reaction. This finding is due to the increased disorder degree of the system during Cu<sup>2+</sup> adsorption.

### 3.5. Adsorption difference and its relationship with physicochemical properties

Fig. 5 shows the adsorption difference for Cu<sup>2+</sup> of unmodified, BS-12-modified, and BS-NZVI-modified soils. The physicochemical properties, mineral content and negative charge adsorption point of the soil determine the adsorption of Cu<sup>2+</sup>. However, natural soil has a weak adsorption capacity because of its low clay content. The BS-12 modification observably improved the adsorption

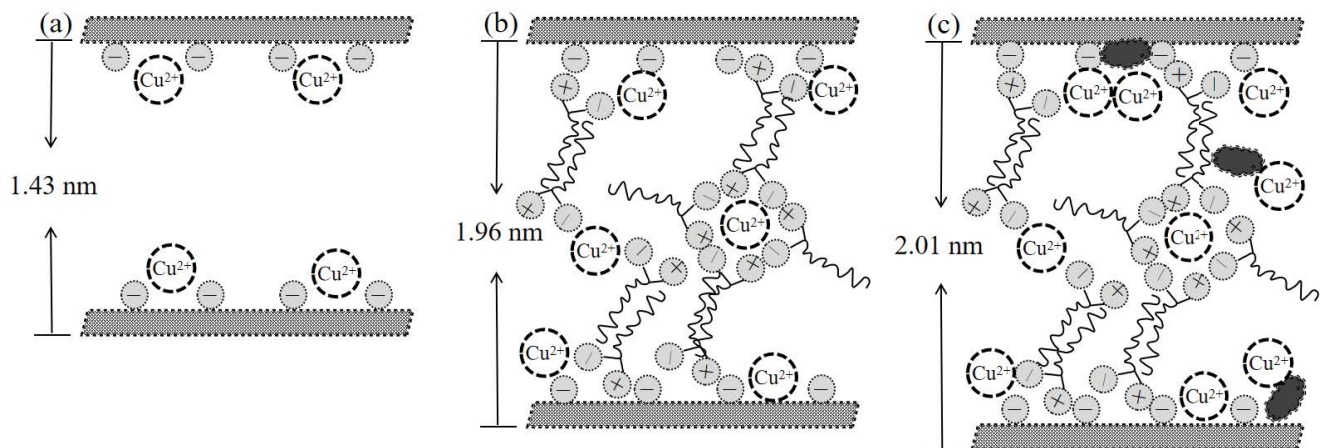


Fig. 5. Difference in Cu<sup>2+</sup> adsorption of unmodified (a), BS-modified (b), and BS-NZVI-modified (c) soils.

Table 3  
Linear fitting diagram between  $q_m$  ( $R_m$ ) and physicochemical properties of soil

Cu content	Physicochemical properties	Regression equation	Correlation coefficient/r
$q_m$	pH	$\text{pH} = -0.001q_m + 8.00$	0.2092
	CEC	$\text{CEC} = -0.159q_m + 150.94$	0.2529
	TOC	$\text{TOC} = 1.435q_m - 116.01$	0.6438 <sup>a</sup>
	$S_{\text{BET}}$	$S_{\text{BET}} = -0.477q_m + 154.66$	0.6383 <sup>a</sup>
$R_m$	pH	$\text{pH} = -0.916R_m + 8.58$	0.2359
	CEC	$\text{CEC} = 148.45R_m - 17.29$	0.3138
	TOC	$\text{TOC} = 128.04R_m + 96.56$	0.0762
	$S_{\text{BET}}$	$S_{\text{BET}} = 2.18R_m + 48.12$	0.0039

<sup>a</sup>indicates that the correlation coefficient is significant at  $p = 0.05$  level ( $r = 0.632$  when the degree of freedom  $f = 8$  and the level of significance  $p = 0.05$ ).

capacity of the natural soil to  $\text{Cu}^{2+}$ , and the amphoteric surface modifier (BS-12) not only had positively and negatively charged hydrophilic groups but also replaced the interlayer exchange cations through interlaminar intercalation, thus entering the soil layer. The long carbon chain of BS-12 can also be combined in the form of a hydrophobic bond [32]. Thus, BS-12 accumulated between layers, the TOC content and crystal spacing of modified soil samples increased accordingly, and the adsorption capacity of  $\text{Cu}^{2+}$  increased. NZVI has strong reducibility and high surface activity. When the BS-12-modified soil was loaded by NZVI, the  $S_{\text{BET}}$  and interlamellar spacing of the BS-NZVI-modified soil increased, and the reducibility of BS-NZVI-modified soil to  $\text{Cu}^{2+}$  improved, which increased the contact opportunity and adsorption effect for  $\text{Cu}^{2+}$ .

Table 3 shows the linear fitting results between  $q_m$ ,  $R_m$  and the physicochemical properties of bank soil.  $q_m$  was significantly positively correlated with TOC and significantly negatively correlated with  $S_{\text{BET}}$ . A poor correlation was observed between  $R_m$  and the physicochemical properties of soil. The above results show that soil TOC and  $S_{\text{BET}}$  play a key role in determining the adsorption effect of  $\text{Cu}^{2+}$  on different amended soils. When the soil was modified by BS-12, the TOC of the soil surface and the number of adsorption points by BS-12 for  $\text{Cu}^{2+}$  increased; the high number of adsorption points resulted in strong ion exchange [33]. In addition, the coverage of BS-12 decreased the  $S_{\text{BET}}$  and occupied the adsorption sites on the soil samples, thus decreasing the  $\text{Cu}^{2+}$  adsorption capacity of the soil sample [29]. Thus, the  $q_m$  of  $\text{Cu}^{2+}$  was negatively correlated with the  $S_{\text{BET}}$  content.

#### 4. Conclusion

- After BS-12 and BS-NZVI modification, the pH, CEC, and  $S_{\text{BET}}$  of riverbank soils decreased, whereas the TOC increased. The surface of riverbank soil modified by BS-12 was loose and smooth. After loading with NZVI, the surface of the soil sample became rough, and NZVI was uniformly distributed.
- In the range of pH 3–5, the influence of pH on the adsorption of  $\text{Cu}^{2+}$  to each sample was non-significant. The adsorption amount of  $\text{Cu}^{2+}$  on the different soil samples (except CX) increased at first and then decreased with the increase in ionic strength.

The adsorption amount of  $\text{Cu}^{2+}$  increased when the temperature increased from 20°C to 40°C.

- The adsorption isotherms of  $\text{Cu}^{2+}$  for BS-12- and BS-NZVI-modified soils were all L-shaped, and the adsorption amount of  $\text{Cu}^{2+}$  by different samples was ranked in the following order: BS-NZVI modification > BS-12 modification > without modification. The adsorption of  $\text{Cu}^{2+}$  by different soil samples was a spontaneous, endothermic and entropy-adding process.
- $q_m$  was significantly correlated with TOC and  $S_{\text{BET}}$  whereas  $R_m$  was poorly correlated with the physicochemical properties of soil.

#### Acknowledgment

The authors wish to acknowledge and thank the Fundamental Research Funds of China West Normal University (17E057), the Scientific Research Foundation of the Education Department of Sichuan Province (18ZB0576) and the financial assistance of the Sichuan Science and Technology Program (2018JY0224).

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