



Adsorption and desorption mechanisms of Cu^{2+} on amended subsurface riverbank soils

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ABSTRACT

To explore the adsorption and desorption mechanisms of Cu^{2+} on different amended subsurface (20–40 cm) riverbank soils, two kinds of modified pomace [i.e., saponified grapefruit pomace (SGP) and saponified orange pomace (SOP)] were added to the subsurface soils of Cangxi, Nanbu, Jialing, and Hechuan from the Jialing River; Santai and Chuanshan from the Fu River; and Quxian and Guangan from the Qu River in Sichuan and Chongqing, China, respectively, at a mass ratio of 5%. Then, the batch method was used to study the isothermal adsorption and desorption characteristics of Cu^{2+} on all the amended soil samples. Furthermore, the morphological changes of Cu^{2+} on the tested soil samples were analyzed. The following results were obtained: (1) The adsorption isotherms of Cu^{2+} on each tested soil sample were “L” type and accorded with the Langmuir adsorption model. The Cu^{2+} adsorption amount of soil samples from the Fu and Jialing rivers was larger than that from the Qu River, and the maximum adsorption capacity was 269.46 mmol/kg (Jialing soil amended by SOP). (2) The stability of Cu^{2+} adsorption on soil samples amended by SGP was stronger than that by SOP, and the maximum desorption rate was less than 22%. The Cu^{2+} adsorption stability of soil samples from the Fu and Jialing rivers was stronger than that from the Qu River. (3) The main existing form of Cu adsorbed by SGP-amended soil was carbonate-bound form, followed by iron–manganese oxidation form. Cu in iron–manganese oxidation form was the highest on SOP-amended soils. (4) Soil pH, cation exchange capacity (CEC), and specific surface area (S_{BET}) were the key factors that determine the Cu^{2+} adsorption amount (S_{BET}) and morphological changes (pH and CEC).

Keywords: Modified pomace; Riverbank soil; Cu^{2+} ; Adsorption and desorption

1. Introduction

With the development of industry and agriculture, the emissions of the “three wastes” (wastewater, waste gas, and waste residue) have seriously damaged the soil environment [1–3], resulting in soil carrying a large amount of pollutants from the environment [4], of which heavy metal

pollution is particularly serious. Heavy metal ions are not only difficult to degrade; they also easily enter the food chain through plant absorption, thereby harming human health [5–9]. Therefore, exploring effective remediation techniques for treating heavy metal-contaminated soil is crucial to protect the soil environment and human health.

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In recent years, natural agricultural and forestry waste, such as straw, waste tea, and fruit residue, have become a major research topic in the field of environmental remediation due to its wide sources, low price, and renewable features [10–12]. Studies have shown that the fruit residue not only contains numerous carboxyl, hydroxyl, and other active functional groups, which can absorb pollutants in the solution [13,14]; it is also rich in cellulose, lignin, polysaccharides and other substances that can complexate and chelate with heavy metals [15,16]. Yu et al. [17] found that the adsorption capacities of bagasse on Cd^{2+} and Pb^{2+} were 0.11 and 0.04 mg/g, respectively. In a solution with an initial concentration of 10 mg/L Cr(VI), the removal rate of Cr(VI) by the pineapple skin biochar material reached more than 80% [18]. Ajmal et al. [19] used natural orange peel to remove nickel ions in electroplating wastewater, and obtained a removal rate of 96%. The saturated adsorption capacity of Cd(II) on biochar prepared by pyrolysis walnut shell at 600°C was 23.79 mg/g [20]. In recent years, researchers have often modified natural materials to improve their adsorption performance to pollutants. Osvaldo et al. [21] found that (ethylene diamine tetraacetic acid) EDTA-modified bagasse can remarkably increase the adsorption capacity of Cu^{2+} , Cd^{2+} , and Pb^{2+} . Studies have shown that the maximum theoretical adsorption value of lemon peel modified by sodium hydroxide for Congo red is 375.37 mg/g [22]. The removal rate of Pb^{2+} and Cd(II) in wastewater by ZnCl_2 or oxalic acid-modified grapefruit peel biosorbent was above 90% [16,23].

Grapefruits and oranges are high-yielding fruits in Sichuan and Chongqing in China, and the discharge of their production residues can easily cause pollution to the environment [24]. If the fruit residue is modified and used to amend the soil samples along rivers, it not only realizes the recycling of environmental waste but also improves the ability of the soil along rivers to adsorb and block runoff pollutants. In this experiment, saponified grapefruit pomace (SGP) and saponified orange pomace (SOP) were added to riverbank soils from Sichuan and Chongqing. Then, the Cu^{2+} isothermal adsorption and desorption characteristics and the morphological changes of Cu^{2+} on different amended soil samples were analyzed to provide a theoretical basis for the application of agricultural and forestry waste in the remediation of soil heavy metal pollution.

2. Materials and methods

2.1. Materials

2.1.1. Preparation of modified pomace

Fresh grapefruit (produced from Tongnan, Chongqing City, China) and orange (produced from Nanchong, Sichuan Province, China) were, respectively, squeezed to obtain fruit pomace, washed with water and dried, crushed, washed with deionized water (dH_2O) several times to remove floating color and impurities, then the samples were dried to a constant weight at 60°C.

50 g of pretreated pomace were placed into a 1 L beaker; 250 mL of anhydrous ethanol and 250 mL of 0.4 mol/L NaOH solution were added. After continuous stirring for 24 h, the modified pomace was obtained after washing several times with dH_2O . Then, it was dried and crushed

before passing through a 60-mesh sieve. Afterward, SGP and SOP were prepared for later use.

2.1.2. Collection of soil along rivers

Eight sampling sites (representative farmland within 50 m from the river) were selected along the three rivers north of Sichuan Province and Chongqing City, China in July 2019; three sites in Jialing River, two sites in Fu River, two sites in Qu River, and one site at the intersection of the three rivers were included. The sampling depth was 20–40 cm (subsurface layer); the samples were named CX (Cangxi), NB (Nanbu), JL (Jialing), HC (Hechuan), ST (Santai), CS (Chuanshan), QX (Quxian), and GA (Guangan) in accordance with the district (county) name letters of the sampling area. After natural air drying, the collected soil samples were removed of animal and plant residues, gravel, and other impurities; then, the samples were ground and passed through a 100-mesh sieve, and their basic physical and chemical properties were determined, respectively (Table 1).

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

2.2. Experimental design

2.2.1. Preparation of amended soil samples

SGP and SOP were added to eight riverbank soils from the three rivers at a mass ratio of 5%. Sixteen amended soil samples were formed and named as CX_{SGP} , NB_{SGP} , JL_{SGP} , HC_{SGP} , ST_{SGP} , CS_{SGP} , QX_{SGP} , GA_{SGP} , CX_{SOP} , NB_{SOP} , JL_{SOP} , HC_{SOP} , ST_{SOP} , CS_{SOP} , QX_{SOP} and GA_{SOP} .

2.2.2. Adsorption and desorption experiments

The preliminary experiment showed that the adsorption isotherm changed when the concentration reached 300–400 mg/L. Therefore, the adsorption isotherms of Cu^{2+} were set at 0, 20, 50, 100, 150, 200, 300, 400, and 500 mg/L. After adsorption, 0.5 mol/L KCl solution was used for desorption.

2.3. Experimental methods

A total of 1 g of tested soil samples were weighed in nine 50 mL plastic centrifuge tubes, and 20 mL of Cu^{2+} solution with different concentration gradients was added into the pipette under the following conditions: constant temperature of 25°C, 150 rpm, and 12 h oscillation (the preliminary kinetic experiments showed that adsorption equilibrium was reached after 12 h) [25]. The supernatant was obtained 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 remaining liquid was poured out from the above nine centrifugal tubes and weighed again. Then, 20 mL of 0.5 mol/L KCl solution was added and oscillated at 25°C for 12 h. The supernatant was centrifuged at 4,800 rpm

Table 1
Basic physical and chemical properties of different soil samples

Rivers	Soil samples	pH values	CEC (mmol/kg)	TOC (g/kg)	Specific surface areas (m ² /g)	Cu content (mg/kg)
Jialing River	CX	8.42	180.93	17.51	122.41	14.64
	NB	7.96	102.73	31.89	114.71	21.36
	JL	7.69	205.76	10.91	128.39	10.37
	HC	6.64	116.54	25.28	83.63	5.38
Fu River	ST	7.68	174.75	15.49	113.25	16.33
	CS	7.52	161.46	5.85	122.41	7.91
Qu River	QX	7.36	86.37	21.50	123.47	12.12
	GA	6.78	110.46	13.59	91.28	40.72

for 20 min. The concentration of the supernatant was determined again to calculate the desorption amount.

The soil samples after adsorption of 500 mg/L Cu²⁺ were analyzed by the Tessier five-step extraction method [26] for the content of various forms of Cu. The Cu²⁺ content was determined via flame atomic absorption spectrophotometry, and background absorption was corrected through the Zeeman effect.

2.4. Data processing

2.4.1. Calculation of equilibrium adsorption amount

The equilibrium adsorption amount was calculated using Eq. (1):

$$q = \frac{V \times (C_0 - C_1)}{W_0} \quad (1)$$

where C_0 (mmol/L) and C_1 (mmol/L) are the initial and equilibrium concentrations of Cu²⁺ in the solution, respectively. V (mL) is the volume of the Cu²⁺ solution added. W_0 (g) is the weight of the tested soil sample. q (mmol/kg) is the equilibrium adsorption amount of Cu²⁺ on the tested soil.

2.4.2. Calculation of desorption amount

The desorption amount was calculated using Eq. (2):

$$d = \frac{[C_2 \times (V + W_2 - W_1)] - [C_1 \times (W_2 - W_1)]}{W_0} \quad (2)$$

where W_1 is the mass (g) of the test soil and centrifuge tube. W_2 is the mass (g) of the test soil, residual liquid, and centrifuge tube. C_2 is the concentration of Cu²⁺ in the filtrate (mmol/L). d (mmol/kg) is the desorption amount of Cu²⁺ on the tested soil.

2.4.3. Fitting of adsorption isotherms

The Langmuir isotherm was selected on the basis of the adsorption isotherm trend [27], and the isothermal equation is as follows:

$$q = \frac{q_m b C_1}{1 + b C_1} \quad (3)$$

where q_m indicates the maximum adsorption amount of Cu²⁺ on the different materials, mmol/kg; b represents the apparent equilibrium constant of the Cu²⁺ adsorption, which can be used to measure the affinity of adsorption.

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 Cu²⁺ by tested soil samples

Fig. 1 shows the adsorption isotherms of Cu²⁺ of different amended riverbank soil samples. The adsorption capacity of different amended soil samples for Cu²⁺ all increased with the increase in equilibrium concentration and eventually tended to be saturated; moreover, it presented "L"-shaped adsorption isotherms. In Table 2, the Langmuir model was used to fit the adsorption isotherms of different tested soil samples to Cu²⁺. The results showed that the fitting correlations reached considerably significant levels, indicating that the model used was suitable for describing the adsorption of Cu²⁺ by the amended soil samples. The maximum adsorption quantity (q_m) of Cu²⁺ on the riverbank soil samples amended by SGP and SOP was changed in 93.49–178.18 and 99.44–269.46 mmol/kg, respectively. Basically, the amended soil samples from the Jialing and Fu rivers have a strong adsorption capacity for Cu²⁺ than the soil from the Qu River. Under the same experimental conditions, the Cu²⁺ adsorption capacity of soil samples amended by SOP was slightly stronger than the soil amended by SGP. Compared with the adsorption results of Cu²⁺ on biochar and clay amended soil [28], the Cu²⁺ adsorption ability of SOP- and SGP-amended soil is improved more.

3.2. Desorption characteristics of different amended soil samples for Cu²⁺

The Cu²⁺ desorption curve of the tested soil sample is shown in Fig. 2. The total desorption amount increased

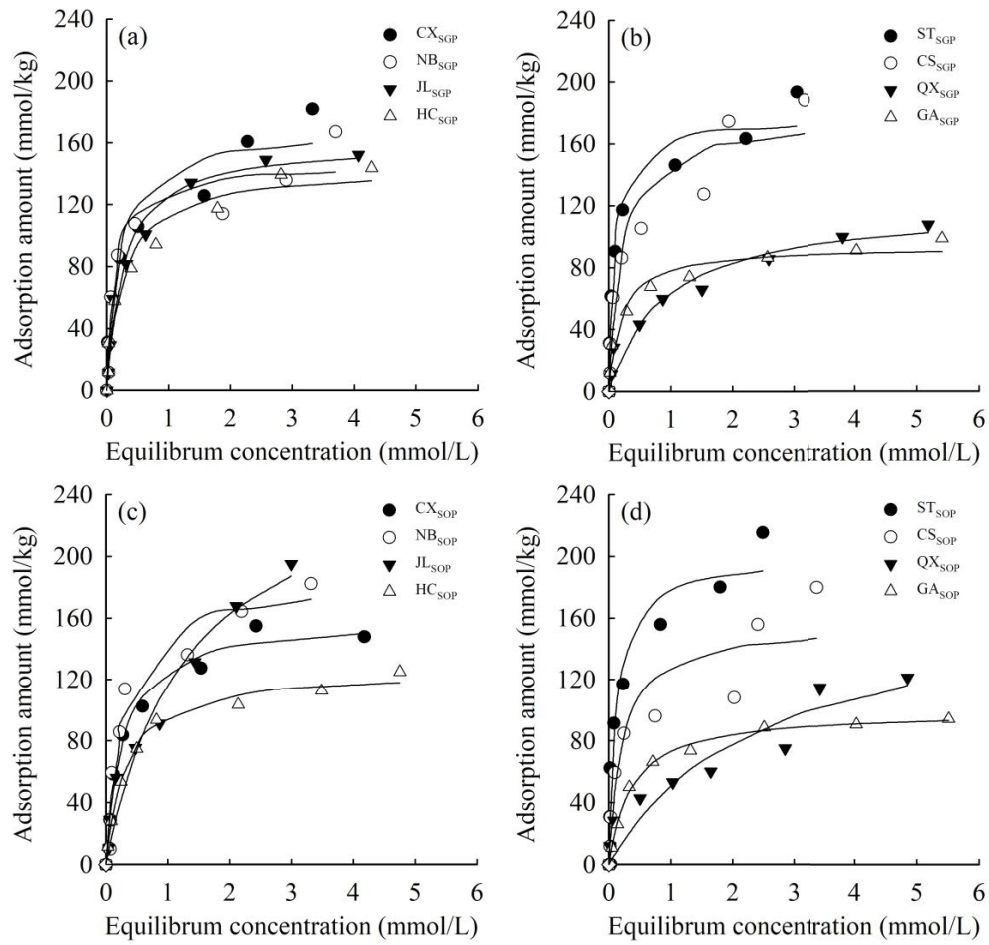


Fig. 1. Adsorption isotherms of Cu²⁺ on different tested soil samples.

Table 2
Langmuir parameters of Cu²⁺ adsorption on tested soil samples

Test soil samples	q_m (mmol/kg)	Correlation coefficient, r	Standard deviation, S	b
CX _{SGP}	169.71	0.9672 ^a	17.54	4.73
NB _{SGP}	146.13	0.9691 ^a	15.22	7.47
JL _{SGP}	160.23	0.9916 ^a	8.09	3.67
HC _{SGP}	144.10	0.9830 ^a	10.53	3.65
ST _{SGP}	176.99	0.9792 ^a	15.05	10.20
CS _{SGP}	178.18	0.9642 ^a	19.27	4.56
QX _{SGP}	120.02	0.9773 ^a	8.64	1.12
GA _{SGP}	93.49	0.9832 ^a	6.96	5.06
CX _{SOP}	160.28	0.9895 ^a	9.03	3.56
NB _{SOP}	187.00	0.9771 ^a	15.22	3.53
JL _{SOP}	269.46	0.9826 ^a	13.69	0.76
HC _{SOP}	126.17	0.9966 ^a	4.02	3.08
ST _{SOP}	200.15	0.9607 ^a	23.27	7.94
CS _{SOP}	155.81	0.9447 ^a	21.69	4.64
QX _{SOP}	173.43	0.9465 ^a	14.73	0.13
GA _{SOP}	99.44	0.9984 ^a	2.19	2.75

Note: *a* 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 $r = 0.765$.

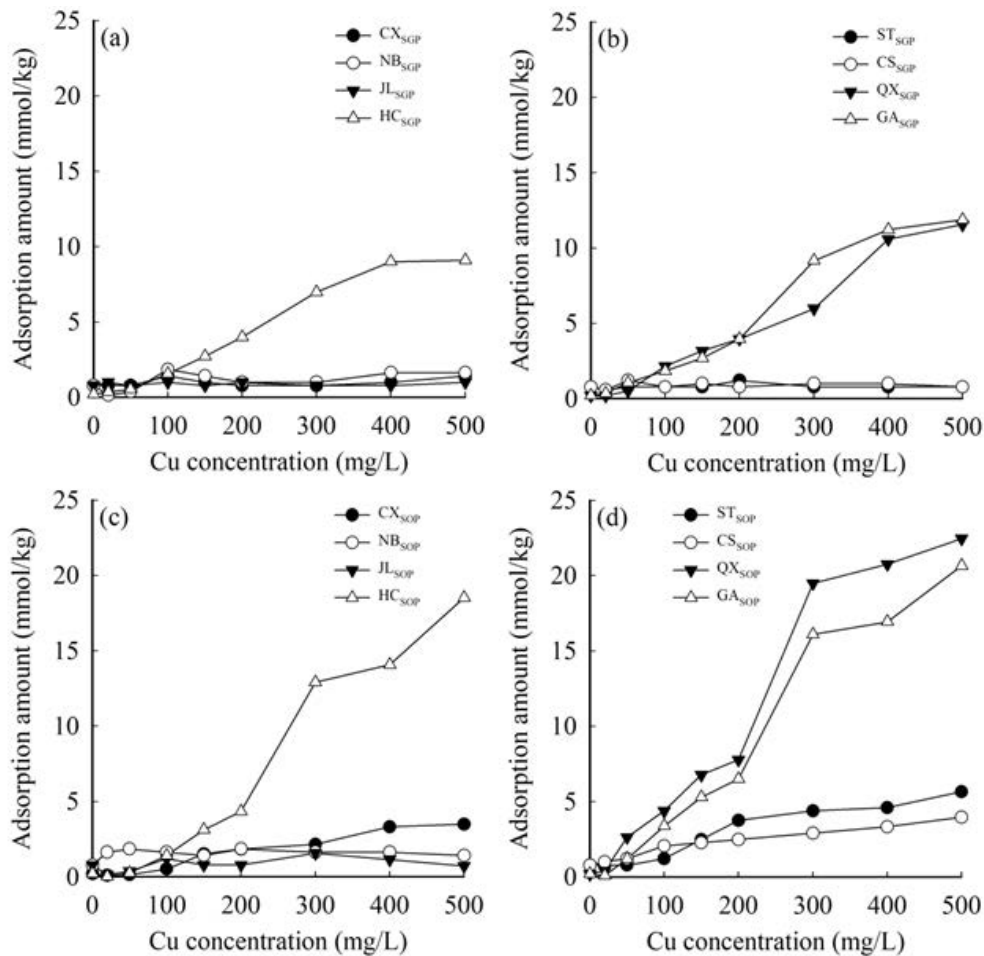


Fig. 2. Desorption amount of Cu^{2+} in different tested soil samples.

with the increase in Cu^{2+} concentration, and the maximum (500 mg/L) desorption amount was 22.45 mmol/kg. The adsorption stability of tested soil samples from the Fu and Jialing rivers (except for HC, the intersection of the three rivers) to Cu^{2+} were higher than that from the Qu River. The adsorption stability of the SGP-amended soil samples to Cu^{2+} is stronger than that of the modified SOP-amended soil samples. Under the condition of Cu^{2+} concentration gradient in 500 mg/L, the desorption amount of Cu^{2+} on SGP-amended soil was generally smaller than that on SOP-amended soil, and the maximum desorption rate was less than 22%. The desorption rate of QX_{SOP} and GA_{SOP} reached up to 18.58% and 21.86%, respectively.

3.3. Adsorption form of Cu in each tested soil sample

The absorbed Cu content in various forms of the tested soil sample were measured, as shown in Fig. 3. The Cu content and proportion in different forms of amended soil samples varied. The SGP-amended soil samples from the Fu River (MY and SN) and the Jialing River (CX, NB, and JL) had the most carbonate-bound Cu content, reaching more than 40% of the total. The SOP-amended soil samples from the three rivers had the most

iron–manganese oxidation Cu content. Under the same conditions, the ratio of Cu in iron–manganese oxidation and ion-exchange form of the soil was higher after being amended by SOP; by contrast, the proportion of the carbonate-bound Cu adsorbed by the SGP soil sample was higher. The exchangeable Cu content showed a gradual increase trend near the Qu River. The carbonate-bound and the iron–manganese oxidation Cu content from the three rivers ranked in the order of Fu River > Jialing River > Qu River. The content of organic Cu in the SGP-amended soil sample was lower than that in SOP-amended soil.

3.4. Relationship between the Cu adsorption and basic physicochemical properties of soil

The correlation between the Cu adsorption on the amended soil and the physical and chemical properties of the soil are shown in Tables 3 and 4. In the amended soil samples, pH, cation exchange capacity (CEC), and S_{BET} had a positive correlation with carbonate and iron–manganese oxidation Cu content but had a negative correlation with exchangeable Cu content; moreover, it had low or irrelevant relationship with organic Cu content. In SGP-amended soil, q_m was significantly and positively correlated with S_{BET} .

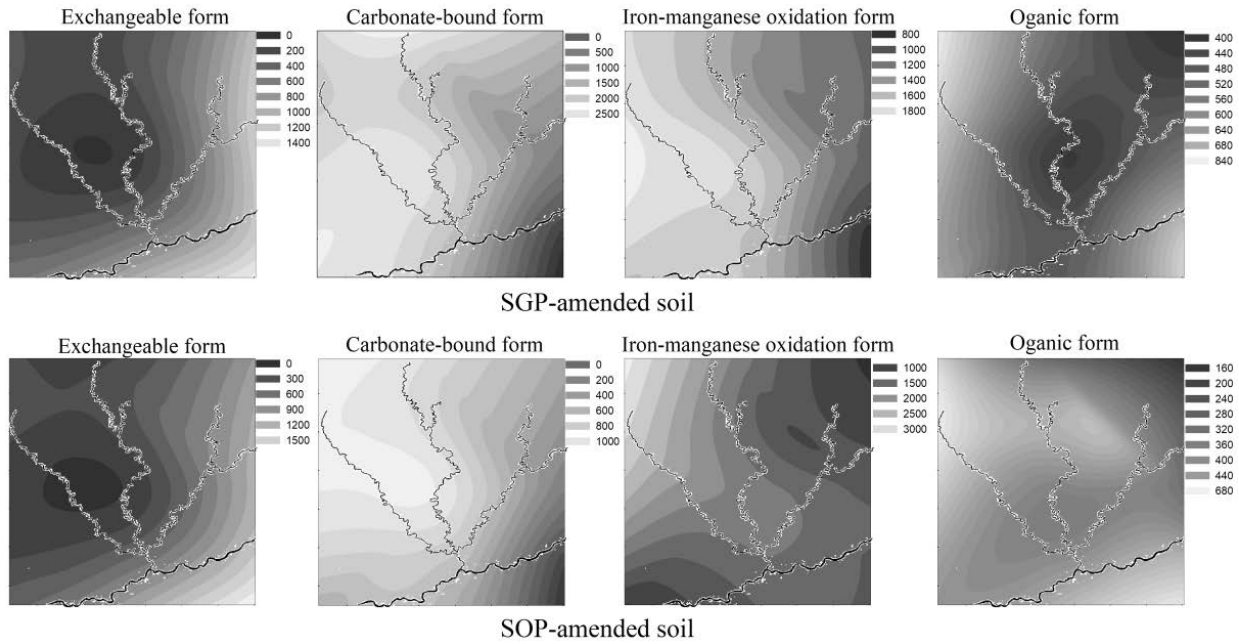


Fig. 3. Cu content in different forms from the three river basins.

Table 3
Correlation between Cu adsorption (SGP-amended soil) and physicochemical properties

Cu content	Physicochemical properties	Regression equation	Correlation coefficient, <i>r</i>	Standard deviation, <i>S</i>
q_m	pH	$pH = 0.01q_m + 5.72$	0.6069	0.50
	CEC	$CEC = 1.08q_m - 17.51$	0.7309 ^a	32.15
	TOC	$TOC = -0.07q_m + 28.58$	0.2602	8.65
	S_{BET}	$S_{BET} = 0.28q_m + 71.58$	0.4999	15.24
Exchangeable form (E_p)	pH	$pH = -0.06E_f + 7.99$	0.7317 ^a	0.43
	CEC	$CEC = -4.87E_f + 180.27$	0.7724 ^a	29.92
	TOC	$TOC = 0.45E_f + 14.28$	0.3721	8.32
	S_{BET}	$S_{BET} = -1.32E_f + 122.73$	0.5613	14.56
Carbonate-bound form (C_p)	pH	$pH = 0.0312C_f + 6.77$	0.7250 ^a	0.44
	CEC	$CEC = 2.70C_f + 78.82$	0.8443 ^b	25.24
	TOC	$TOC = -0.25C_f + 23.66$	0.4136	8.16
	S_{BET}	$S_{BET} = 0.70C_f + 95.97$	0.5858	14.26
Iron–manganese oxidation form (IM_p)	pH	$pH = 0.04IM_f + 6.63$	0.2900	0.61
	CEC	$CEC = 8.05IM_f - 36.91$	0.7934 ^a	28.67
	TOC	$TOC = -0.94IM_f + 38.69$	0.4871	7.82
	S_{BET}	$S_{BET} = 1.13IM_f + 87.24$	0.2985	16.80
Organic form (O_p)	pH	$pH = -0.05O_f + 7.93$	0.1392	0.63
	CEC	$CEC = -0.03O_f + 142.66$	0.0013	47.10
	TOC	$TOC = -0.54O_f + 22.32$	0.1073	8.91
	S_{BET}	$S_{BET} = -2.90O_f + 136.80$	0.2912	16.84

Note: *a* and *b* indicate a significant correlation at the level of $p = 0.05$ or 0.01 . When $f = 7$, and $p = 0.05$ or 0.01 , $r = 0.666$ or 0.798 .

Exchangeable and carbonate Cu were significantly correlated with pH and CEC. Iron–manganese oxide Cu was significantly correlated with CEC. A similar correlation was found among the Cu and physicochemical properties

of SOP-amended soil. Therefore, pH, CEC, and S_{BET} are the key factors that affect the adsorption of Cu by the test soil. The above results were obtained because the CEC of the soil surface could provide the number of adsorption point sites

Table 4
Correlation between Cu adsorption (SOP-amended soil) and physicochemical properties

Cu content	Physicochemical properties	Regression equation	Correlation coefficient, r	Standard deviation, S
q_m	pH	$\text{pH} = 0.01q_m + 6.47$	0.5288	0.54
	CEC	$\text{CEC} = 0.50q_m + 56.52$	0.5868	38.14
	TOC	$\text{TOC} = -0.02q_m + 21.13$	0.1215	8.89
	S_{BET}	$S_{\text{BET}} = 0.23q_m + 73.01$	0.7214 ^a	12.19
Exchangeable form (E_f)	pH	$\text{pH} = -0.0593E_f + 8.00$	0.7687 ^a	0.40
	CEC	$\text{CEC} = -4.58E_f + 180.43$	0.7989 ^b	28.33
	TOC	$\text{TOC} = 0.49E_f + 13.71$	0.4460	8.01
	S_{BET}	$S_{\text{BET}} = -1.43E_f + 124.32$	0.6670 ^a	13.11
Carbonate-bound form (C_f)	pH	$\text{pH} = 0.07C_f + 6.80$	0.7139 ^a	0.44
	CEC	$\text{CEC} = 6.27C_f + 80.89$	0.8294 ^b	26.31
	TOC	$\text{TOC} = -0.44C_f + 22.08$	0.3067	8.53
	S_{BET}	$S_{\text{BET}} = 1.56C_f + 97.17$	0.5516	14.68
Iron–manganese oxidation form (IM_f)	pH	$\text{pH} = 0.02IM_f + 7.04$	0.2663	0.61
	CEC	$\text{CEC} = 3.27IM_f + 62.00$	0.6136	37.19
	TOC	$\text{TOC} = -0.35IM_f + 26.47$	0.3499	8.39
	S_{BET}	$S_{\text{BET}} = 0.28IM_f + 105.47$	0.1425	17.42
Organic form (O_f)	pH	$\text{pH} = -0.09O_f + 8.09$	0.2941	0.61
	CEC	$\text{CEC} = -2.62O_f + 160.27$	0.1205	46.76
	TOC	$\text{TOC} = 1.44O_f + 7.91$	0.3487	8.39
	S_{BET}	$S_{\text{BET}} = -4.37O_f + 142.32$	0.5387	14.83

Note: *a* and *b* indicate a significant correlation at the level of $p = 0.05$ or 0.01 . When $f = 7$, and $p = 0.05$ or 0.01 , $r = 0.666$ or 0.798 .

for Cu, and the more the number of point sites, the stronger the ion exchange effect [29,30]. The content of total organic carbon (TOC) in the soil sample would occupy the adsorption point of the tested soil sample [31], thus inhibiting the adsorption capacity of the tested soil sample to Cu, and the Cu adsorption amount of the soil sample was negatively correlated with TOC content.

4. Conclusion

- The adsorption isotherms of Cu^{2+} on different amended soils are all “L” shaped, and they accorded with the Langmuir model. Soil samples from the Fu and Jialing rivers presented stronger Cu^{2+} adsorption ability than those from the Qu River.
- The adsorption stability of Cu^{2+} by SGP-amended soils was stronger than that of soil SOP-amended bank soils, and the maximum desorption rate was less than 22%.
- The main existing form of Cu adsorbed by SGP-amended soil was carbonate-bound form, followed by iron–manganese oxidation form. Cu in iron–manganese oxidation form was the highest on SOP-amended soils.
- The influence of pH, CEC, and S_{BET} on Cu adsorption by different amended soils was greater than that of TOC.

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