Effects of soil components, solution chemical properties, and temperature on Cu(II) adsorption by alluvial acid soil: A case study in Southwest China

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Abstract

The specific soil components such as soil organic matter, Fe and Mn oxides exert a significant influence on Cu(II) adsorption in soil. In the present study, clay fraction was separated from an alluvial acid soil, then the selective chemical extraction method was used to remove the specific components in the bulk soil and clay fraction. Adsorption experiments showed that the adsorption capacity of the clay fraction of Cu(II) is greater than that of the bulk soil, regardless of whether it is treated by selective chemical extraction or not. Compared with untreated soil samples, after the removal of organic matter by H$_2$O$_2$, $K_d$ decreased by a maximum of 82.8% for the bulk soil and 73.5% for the clay fraction. After the removal of manganese oxides by NH$_2$OH·HCl, $K_d$ decreased by a maximum of 68.1% for the bulk soil and 73.2% for the clay fraction. However, after the removal of free iron oxides by dithionite-citrate-bicarbonate, $K_d$ increased by a maximum of 422% for the bulk soil and 195.5% for the clay fraction. $K_d$ increased by 4263.3% when the initial pH increased from 2 to 3.5 and, then, increased to 6. The amount of Cu(II) adsorbed did not change significantly. Within a range greater than 6, the increased Cu(II) adsorption may be due to the precipitation of Cu(II). When the concentration of NaNO$_3$ changes from 0.01 to 0.1 M, the adsorption capacity decreased by a maximum of 36%, $K_d$ decreased by a maximum of 84.3%. The presence of foreign ions decreased Cu(II) adsorption; their order of effect on Cu(II) adsorption is Na$^+$ < K$^+$ < Mg$^{2+}$ < Ca$^{2+}$ for cations and NO$_3^-$ < SO$_4^{2-}$ ≈ Cl$^-$ for anions. The adsorption of Cu(II) was an endothermic and spontaneous process under the experimental conditions.

1. Introduction

Cu is an abundant element in the lithosphere. It is also an essential metal for plant nutrition (He et al., 2005). Cu is present in limestone, poultry waste, phosphate fertilizer, agrochemical products, and sludge. When the concentration of Cu in soil solution is very high, it is toxic to plants and detrimental to the environment and ultimately affects human health (Silveira et al., 2002; Andrade et al., 2005). The solubility of copper in soil solutions is controlled by adsorption/desorption, complexation, and precipitation. These interactions determine the mobility and bioavailability of Cu(II) in soil and water environments (Silveira et al., 2003; Violante et al., 2010).

Soil is a heterogeneous medium composed of different components (i.e., clay minerals, soil organic matter, and iron/manganese oxides). Due to the differences in surface characteristics, the adsorption capacity of these components for metal ions is also different. Amorphous oxides and organic matter are the primary factors controlling copper adsorption (Parat et al., 2002). The transformation and enrichment of organic matter significantly influence the chemical mobility and retention of copper in paddy soil (Wang et al., 2009a). Additionally, because of the differences in specific surface area, Fe/Mn/Al oxides and organic matter contents (Acosta et al., 2009; Bi et al., 2013), the adsorption capacity of various particle size aggregates is also different (Acosta et al., 2011); this property also depends on the heavy metal/metalloid species (Huang et al., 2017).
The adsorption of Cu(II) is also affected by the chemical properties of the soil solution (i.e., pH, foreign ions, ionic strength, etc.) (Dai et al., 2017). In general, pH can affect the speciation of metal ions through hydrolysis reactions and, thus affect the adsorption performance of metal ions (Yun, et al., 2001; Sheng et al., 2011). Ionic strength can affect the solution-phase activity of metals, number of competing ions, and properties of the electric double layer (Baker, et al., 2009; Zhou et al., 2010). Foreign cations can compete with metal ions for adsorption sites. Due to the differences in the valence and hydration ratios of foreign cations, their influence on the adsorption of metal ions varies (Guo et al., 2011). Foreign anions (i.e., NO\textsuperscript{-3}, SO\textsubscript{4}\textsuperscript{2-}, Cl\textsuperscript{-}, or ClO\textsubscript{4}\textsuperscript{-}) can form anion-soluble metal–water complexes with metal ions; this complexation is affected by the radius and other properties of foreign anions (Wang et al., 2009b).

To date, the effects of specific components and solution chemical properties on the adsorption of Cu(II) onto alluvial acid soil have not yet been thoroughly investigated. Therefore, the aims of this study were to (1) investigate the effects of specific components of the alluvial acid soil (clay fraction, organic matter, free iron oxides, and manganese oxides) on Cu(II) adsorption; (2) explore the influence of pH, foreign ions, and ionic strength on Cu(II) adsorption, and (3) evaluate the thermodynamic processes of Cu(II) adsorption.

2. Materials And Methods

2.1. Study site and Soil characterization

The sampling site is located in a farmland area near a coal mine in Sichuan province, southwest China (Fig. 1). The soil is alluvial acid soil. The topsoil samples (0–20 cm) were collected, air dried, crushed, and passed through a 2-mm nylon mesh.

The pH was determined under the soil:water ratio of 1:2.5(w/w) using a pH meter; the organic matter was determined by the K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} oxidation method (Pansu et al., 2006). The contents of free iron oxides and manganese oxides were determined by the dithionite-citrate-bicarbonate (DCB) method (Kunze et al., 1986) and the NH\textsubscript{2}OH·HCl method (Wang et al., 2011), respectively. The cation exchange capacity (CEC) was determined according to ISO 23470. The grain-size distribution was determined according to GBT50123-1999. After digestion by HNO\textsubscript{3}–HF–HClO\textsubscript{4} method, the Cu(II) and iron/manganese contents of the soil were analyzed by inductively coupled plasma source mass spectrometry and atomic absorption spectrophotometry, respectively.

The main characteristics of the studied soil were as follows: clay content was 33.2%, silt content was 54.6%, sand content was 12.2%, pH was 5.28, soil organic matter was 1.84%, CEC was 8.575 mmol kg\textsuperscript{-1}, and the contents of free iron oxides and total iron were 25.76 g kg\textsuperscript{-1} and 41.91 g kg\textsuperscript{-1}, respectively. The total manganese content was 1.01 g kg\textsuperscript{-1} and the Cu(II) content was 28.7 mg kg\textsuperscript{-1}.

2.2 Adsorption experiments
The clay fraction (< 2 µm) samples were separated from the studied soil. Before fractionation, 100 g of soil were immersed overnight in a glass beaker containing 1000 mL of deionized water and later dispersed with ultrasonic (energy was set to approximately 100 J/ml) (Schmidt et al., 1999). Subsequently, natural sedimentation and siphoning were conducted using Stock's Law. The separated sample was centrifuged and naturally dried. Selective extraction technology was employed to remove specific components (organic materials, free iron oxides and manganese oxides) of the bulk soil and clay fraction. In the experiment, 30% of H₂O₂ was used to remove organic materials (Wu et al., 2012); the 0.3 M Na₃C₆H₅O₇·2H₂O + 1MNaHCO₃ + Na₂S₂O₄ (DCB) method was used to remove free iron oxides (Wang et al., 2009a) and 0.1 M HONH₃Cl(pH = 2) removed manganese oxides (Wang et al., 2011).

All adsorption experiments were carried out in 50-mL polyethylene centrifuge tubes on a thermostatic oscillator with an oscillating speed of 180 rpm. The Cu(II)-containing solution was prepared with Cu(NO₃)₂·3H₂O. The pH of the solutions was adjusted using HNO₃ and NaOH. After the adsorption experiment, the solution was centrifuged at 6000 rpm for 20 min and then filtered. The content of Cu(II) in the supernatant was determined using an atomic absorption spectrophotometer. relative errors in the experimental data (p < 5%).

2.3 Experimental data analysis

The amounts of elements adsorbed onto soil were calculated using the following equations (Kumar et al., 2009):

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  
\[ q_t = \frac{(C_0 - C_t)V}{m} \]

where \( q_e \) and \( q_t \) are the amounts of Cu(II) adsorbed at equilibrium and time \( t \), respectively (mg kg⁻¹); \( C_0 \), \( C_e \), and \( C_t \) are the initial, equilibrium, and time \( t \) concentrations of Cu(II) in the solution (mg L⁻¹); \( V \) is the volume of the solution (L); \( m \) is the dry weight of soil (kg); and \( t \) is the adsorption reaction time (min).

The distribution coefficient (\( K_d \)) represents the ratio of the concentration of Cu(II) in the solid phase to that in the liquid phase after a certain adsorption time (Eq. 3); the larger the \( K_d \), the easier the adsorbate is adsorbed by the adsorbent and the less migratory adsorbate is.

\[ K_d = \frac{q_e}{C_e} = \frac{(C_0 - C_e)V}{mC_e} \]

The thermodynamic parameters of the adsorption of Cu(II) onto the soil, i.e., the standard entropy \( \Delta S^0 \), enthalpy \( \Delta H^0 \), and Gibbs free energy \( \Delta G^0 \), were calculated using the van’t Hoff equation (Eq. 4, Eq. 5) (Wang et al., 2013).

\[ \ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  
\[ \Delta G^0 = -RT \ln K_d \]
where $R$ is the ideal gas constant (8.3145 J/mol/K) and $T$ (K) is the Kelvin temperature. $\Delta H^0$ and $\Delta S^0$ were calculated from the plot of $\ln K_d$ versus $1/T$.

### 3. Results And Discussion

#### 3.1 Soil characterization

##### 3.1.1 XRD

Figure 2 shows the X-ray diffraction pattern of the soil. The crystal phase of the bulk soil is composed mainly of quartz, feldspar, and muscovite. For the clay fraction, the peak of feldspar disappeared and the peak intensities of quartz and muscovite weakened; however, the characteristic peaks of clay minerals are still not obvious. This may be because the clay minerals are covered by some amorphous components, masking its characteristic peaks.

##### 3.1.2 FTIR

The FT-IR spectra of the bulk soil and clay fraction are shown in Fig. 3. The absorption peak at 3620 cm$^{-1}$ is due to O–H related to free water (Liu et al., 2011), while the peak at 1630 cm$^{-1}$ corresponds to the aromatic and carboxylate asymmetric stretching (Farinella et al., 2007). The pronounced peak at 1030 cm$^{-1}$ is attributed to Si–O (Madejova et al., 2003) and the sharp peaks at 797 cm$^{-1}$ and 779 cm$^{-1}$ are attributed to quartz. The peak at 533 cm$^{-1}$ corresponds to Al–O–Si, which may indicate the presence of montmorillonite (Yang et al., 2009).

##### 3.1.3 SEM

Fig4(a) shows that the bulk soil contains a large number of tiny pores with complex components and different shapes that are uneven. Figure 4(b) shows the EDS analysis result, in which the primary elements of bulk soil are Si and O, with some areas showing high Al content, indicating that parts of the quartz surface are covered with Al-containing components. Figure 4(c) shows a general view of the clay fraction. The main visible clay particles are flaky minerals with irregular shapes, whose particle sizes are mostly less than 2 µm. Figure 4(d) shows the energy dispersive X-ray (EDX) analysis result, in which the main elements of the clay particles are Si, O, and Al.

#### 3.2. Effect of soil components

##### 3.2.1 Organic matter

Organic matter contains a vast variety of functional groups such as carboxyl, carbonyl, and phenolic groups (Guo et al., 2006), which can affect metal ion adsorption, migration, and transformation behavior in soil. The adsorption capacity of Cu(II) onto the bulk soil and clay fraction decreased after the removal of organic matter. For the bulk soil, as seen in Fig. 5(a), the adsorption capacity of Cu(II) decreased by a maximum of 53.6% ($C_0$:10 mg L$^{-1}$) and a minimum of 11.7% ($C_0$:100 mg L$^{-1}$). For the clay fraction, as
seen in Fig. 5(b), the adsorption capacity of Cu(II) decreased by a maximum of 35.8% ($C_0$:50 mg L$^{-1}$) and a minimum of 10.3% ($C_0$:200 mg L$^{-1}$); the adsorption capacity of Cu(II) onto the clay fraction was larger than that onto the bulk soil. After the removal of soil organic matter, for the bulk soil, $K_d$ decreased by a maximum of 82.8% ($C_0$:10 mg L$^{-1}$) and a minimum of 14.8% ($C_0$:100 mg L$^{-1}$) (Table 1). For the clay fraction, $K_d$ decreased by a maximum of 73.5% ($C_0$:10 mg L$^{-1}$) and a minimum of 15.9% ($C_0$:200 mg L$^{-1}$) (Table 2). The $K_d$ of Cu(II) absorbed by the clay fraction is larger than that of the bulk soil. Other studies have also reported that the adsorption capacity of bulk soil (Agbenin et al., 2004) and different particle-size fractions (Wang et al., 2009a) to Cu(II) decreased after the removal of soil organic matter.

### Table 1
Kd of Cu(II) adsorption after removal of specific components of bulk soil

| $C_0$ (mg L$^{-1}$) | untreated soil | Removal |
|---------------------|----------------|---------|
|                     |                | OM | Fe$_d$ | Mn |
|                     | (L kg$^{-1}$)  |    |        |    |
| 10                  | 636.1          | 109.1 | 3321.1 | 235.7 |
| 30                  | 162.4          | 79.5  | 358.2  | 51.8  |
| 50                  | 119.6          | 77.5  | 201.2  | 44.5  |
| 70                  | 87.5           | 66.2  | 157.6  | 35.4  |
| 100                 | 63.5           | 54.1  | 101.9  | 32.9  |
| 200                 | 46.3           | 39.1  | 59.2   | 26.3  |
### Table 2
Kd of Cu adsorption after removal of specific components of clay fraction

| C₀ (mg L⁻¹) | untreated clay | Removal | OM (L kg⁻¹) | Fe_d | Mn |
|--------------|----------------|---------|-------------|------|----|
| 10           | 1149.5         | 304.5   | 3397.1      | 337.9|    |
| 30           | 436.3          | 161.9   | 613.7       | 116.9|    |
| 50           | 346.7          | 137.3   | 475.9       | 111.2|    |
| 70           | 235.9          | 130.4   | 334.0       | 94.0 |    |
| 100          | 182.9          | 115.3   | 250.8       | 82.3 |    |
| 200          | 130.2          | 109.5   | 195.8       | 93.4 |    |

### 3.2.2 Free iron oxides

Iron oxides and iron (oxy-) hydroxides act as sinks (i.e., Fe nodules and rohrensteins) for heavy metals and metalloids, thereby controlling their mobility in soil and groundwater environments (Cornell et al., 2003; Vodyanitskii et al., 2009). However, after the removal of free iron oxides by the DCB method, the adsorption capacity of Cu(II) onto the bulk soil and clay fraction increased. For the bulk soil, as shown in Fig. 5(a), the adsorption capacity of Cu(II) increased by a maximum of 43.2% (C₀:30 mg L⁻¹) and a minimum of 21.4% (C₀:200 mg L⁻¹). For the clay fraction, as shown in Fig. 5(b), adsorption capacity increased by a maximum of 25.5% (C₀:200 mg L⁻¹) and a minimum of 10% (C₀:30 mg L⁻¹). The Kd increased by a maximum of 422% (C₀:10 mg L⁻¹) and a minimum of 27.7% (C₀:200 mg L⁻¹) for the bulk soil (Table 1); Kd increased by a maximum of 195.5% (C₀:10 mg L⁻¹) and a minimum of 37.1% (C₀:100 mg L⁻¹) for the clay fraction (Table 2). The Kd of adsorption of Cu(II) onto the clay fraction was larger than that onto the bulk soil at the same initial concentration. After the removal of free iron oxides by the DCB method, the adsorption capacity of Cu(II) increased, possibly because the iron oxides are usually present on the surface of clay minerals and the removal of Fe oxides can expose the adsorption sites of clay minerals (Wu et al., 1999). It is also possible that the remaining citrate can form complexes with Cu(II), which may have a strong affinity for soil (Agbenin et al., 2004).

### 3.2.3 Manganese Oxides

In the supergene environment, manganese is primarily present as oxides, which usually form a black crust or coat and are fixed on the surface of rock or soil particles or filled in cracks (Liu et al., 1984). They usually have larger specific surface areas and strongly acidic sites and greatly affect the migration and transformation of heavy metals in the soil through adsorption, The adsorption of heavy metals onto
manganese oxides is primarily considered as special adsorption (Spark et al., 1995). After the removal of manganese oxides, for the bulk soil (Fig. 5(a)), the adsorption capacity of Cu(II) decreased by a maximum of 54.1% (C_0:30 mg L^{-1}) and by a minimum of 28.9% (C_0:10 mg L^{-1}). For the clay fraction (Fig. 5(b)), the adsorption capacity decreased by a maximum of 46.2% (C_0:30 mg L^{-1}) and a minimum of 19.3% (C_0:200 mg L^{-1}). After the removal of manganese oxides, for the bulk soil, K_d decreased by a maximum of 68.1% (C_0:30 mg L^{-1}) and a minimum of 43.2% (C_0:200 mg L^{-1}) (Table 1). For the clay fraction, K_d decreased by a maximum of 73.2% (C_0:30 mg L^{-1}) and a minimum of 28.3% (C_0:200 mg L^{-1}) (Table 2).

3.3 Effect of solution chemical properties

3.3.3 Initial pH

The pH value not only affects the chemical properties of metal ions through precipitation, hydrolysis, complexation, and redox reactions but also the surface properties of the mineral in the soil (Esposito et al., 2002; Yang et al., 1999). The dominant speciation of Cu (Cu^{2+}, Cu(OH)^{+}, Cu_2(OH)_2^{2+}, and Cu(OH)_2^{0}) in a solution corresponds to different pH ranges, which indirectly affects the adsorption of Cu(II) (Li et al., 2009). As Fig. 6 shows, when the pH increased from 2 to 3.5, the Cu(II) adsorption increased rapidly. from 77.3 to 520.5 mg/kg, i.e., by 573.3%. The K_d increased from 3.0 to 130.9 L/kg, i.e., by 4263.3%. This may be because H_3O^{+} gradually leaves the adsorption sites of the adsorbent and is replaced by Cu(II). This process is similar to ion-exchange interactions (H^{+}/Cu^{2+}) (Singh et al., 1993). When the pH ranged between 3.5 and 6, the Cu(II) adsorption did not change significantly. However, when the pH was greater than 6, the adsorption capacity of Cu(II) increased again; this may be due to the precipitation of Cu(OH)_2, which led to the increase in Cu(II) adsorption. Owing to the soil buffering power (i.e., ion exchange of soil colloid, dissociation of strong base and weak acid salt, etc.), the pH of the equilibrated solution tends toward the actual pH of the studied soil.

Ionic strength can affect the number of competing ions and the activity of metal ions in the solution, the interface potential, and the properties of the electric double layer (Zhou, et al., 2010; Baker, et al., 2009). As shown in Fig. 7 and Table 3, ionic strength has a significant effect on Cu(II) adsorption; it decreases with the increasing ionic strength. When the concentration of NaNO_3 changes from 0.01 to 0.1 M, the adsorption capacity decreased by a minimum of 4.9% (C_0:10 mg L^{-1}) and a maximum of 36% (C_0:200 mg L^{-1}), K_d decreased by a minimum of 63.5% (C_0:100 mg L^{-1}) and a maximum of 84.3% (C_0:30 mg L^{-1}). For the same ionic strength, K_d decreased with the increase in the initial concentration of Cu(II) (Table 4).

3.3.1 Ionic strength
Table 3
adsorption capacity (mg kg$^{-1}$) of Cu(II) at different ionic strength

| $C_0$ (mg L$^{-1}$) | ionic strength |
|---------------------|----------------|
|                     | 0.001M | 0.01M | 0.1M |
| 10.0                | 197.6  | 194.9 | 187.9 |
| 30.0                | 575.2  | 556.7 | 470.6 |
| 50.0                | 886.7  | 878.1 | 682.2 |
| 70.0                | 1161.2 | 1111.7| 830.0 |
| 100.0               | 1449.0 | 1399.5| 979.6 |
| 200.0               | 2050.0 | 1969.3| 1310.0|

Table 4
Kd of Cu(II) adsorption under different ionic strength

| $C_0$ (mg L$^{-1}$) | ionic strength |
|---------------------|----------------|
|                     | 0.001M | 0.01M | 0.1M |
| 10.0                | 1664.9 | 760.0 | 310.4 |
| 30.0                | 464.3  | 258.3 | 72.7  |
| 50.0                | 156.5  | 144.0 | 42.9  |
| 70.0                | 97.3   | 77.1  | 29.1  |
| 100.0               | 52.6   | 46.6  | 19.2  |
| 200.0               | 21.0   | 19.4  | 9.7   |

3.3.2 Foreign ions

Natural soil pore water contains different types of electrolytes owing to the different sources and water quality, which also affect the adsorption of metal ions in soil (Boudrahem et al., 2011). As shown in Fig. 8 and Tables 5 and 6, the adsorption capacity and $K_d$ of Cu(II) adsorption are the lowest when the foreign cation is Ca. The order of effect of foreign cations on Cu(II) adsorption is Ca$^{2+}$ > Mg$^{2+}$ > K$^+$ > Na$^+$. The reason why bivalent ions (Ca$^{2+}$ and Mg$^{2+}$) have a greater effect than monovalent ions (K$^+$ and Na$^+$) is likely that bivalent ions have a stronger ability to compete for adsorption sites than monovalent ions.
(Naidu et al., 1994). Additionally, because the hydration radius of $K^+ = 2.32 \text{ Å} < Na^+ = 2.76 \text{ Å}$ (Guo et al., 2011), the effect of $K^+$ on Cu(II) adsorption is more evident than that of $Na^+$.

The order of effect of foreign anions on Cu(II) adsorption is $\text{Cl}^- \approx \text{SO}_4^{2-} > \text{NO}_3^-$. This may be because $\text{SO}_4^{2-}$ and $\text{Cl}^-$ are more likely to form complexes with Cu(II) than $\text{NO}_3^-$ in aqueous environments (Wang et al., 2009b). However, Yang et al. (2006) found that the types of background anions (Cl, NO$_3$, ClO$_4$, NO$_2$, SO$_3$, and PO$_4$) do not affect the adsorption amounts and adsorption trends of Cu(II).

**Table 5**

| $C_0$ (mg L$^{-1}$) | foreign ions |
|---------------------|--------------|
|                     | $K^+$ | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ |
| 10                  | 169   | 195    | 160       | 163       | 172    | 195       | 167         |
| 30                  | 482   | 557    | 413       | 429       | 534    | 557       | 516         |
| 50                  | 672   | 878    | 543       | 574       | 782    | 878       | 757         |
| 70                  | 825   | 1112   | 660       | 735       | 1040   | 1112      | 970         |
| 100                 | 1014  | 1399   | 800       | 867       | 1265   | 1399      | 1199        |
| 200                 | 1505  | 1969   | 1020      | 1140      | 1884   | 1969      | 1921        |

**Table 6**

| $C_0$ (mg L$^{-1}$) | foreign ions |
|---------------------|--------------|
|                     | $K^+$ | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ |
| 10                  | 108   | 760    | 79.9      | 89.1      | 121    | 760       | 100         |
| 30                  | 81.8  | 258    | 44.3      | 50.3      | 162    | 258       | 123         |
| 50                  | 40.9  | 144    | 23.7      | 26.9      | 71.8   | 144       | 62.3        |
| 70                  | 28.7  | 77.1   | 17.9      | 22.1      | 57.7   | 77.1      | 45          |
| 100                 | 20.6  | 46.6   | 13.3      | 15.3      | 34.4   | 46.6      | 30          |
| 200                 | 12.1  | 19.4   | 6.8       | 8.0       | 17.8   | 19.4      | 18.5        |

### 3.4 Effect of temperature
The adsorption experiments were conducted under two initial concentrations of Cu(II) (50 mg L\(^{-1}\) and 100 mg L\(^{-1}\)) and three temperature conditions (293.15, 301.15, and 313.15 K). As shown in Fig. 9, the increase in temperature is conducive to the adsorption of Cu(II). High temperatures can accelerate the diffusion rate of sorbate in aqueous solutions (Gregorio et al., 2008), thus increasing the adsorption of Cu(II).

The values are tabulated in Table 7. A positive \(\Delta H^0\) value and a negative \(\Delta G^0\) value indicate that the adsorption was an endothermic and spontaneous process under the experimental conditions. Furthermore, \(\Delta G^0\) decreased with increasing temperature, indicating that the adsorption process was more efficient at high temperatures. The values of \(\Delta S^0\) are positive, indicating that the soil has a good affinity for Cu(II) in the solution and some structural changes may occur in the adsorbents (Genc-Fuhrman et al., 2004).

| \(C_0\) (mg L\(^{-1}\)) | \(\Delta S^0\) (J·mol\(^{-1}\)·k\(^{-1}\)) | \(\Delta H^0\) (kJ·mol\(^{-1}\)) | \(\Delta G^0\) (kJ·mol\(^{-1}\)) |
|----------------|----------------|----------------|----------------|
| Cl: 50 mg L\(^{-1}\) | 59.37 | 8.13 | 293.15 -9.28 301.15 -9.75 313.15 -10.46 |
| Cl: 100 mg L\(^{-1}\) | 53.76 | 7.51 | 293.15 -8.25 301.15 -8.69 313.15 -9.33 |

### 4. Conclusions

Based on the experimental results, the following conclusions can be drawn:
1. The adsorption capacity of the clay fraction to Cu(II) is greater than that of bulk soil; the removal of soil organic matter and manganese oxides decreases the Cu(II) adsorption capacity for both the bulk soil and clay fraction. However, the opposite trend was observed for free iron oxide removal.
2. As the pH increased, the adsorption increased rapidly and, then, tended toward equilibrium. When the pH was greater than 6, Cu(II) started to precipitate.
3. At the same initial concentration of Cu(II), Cu(II) adsorption decreased with an increase in ion strength.
4. The effect of foreign bivalent cations on the adsorption of Cu(II) is greater than that of monovalent cations. Cl\(^-\) and SO\(_4^{2-}\) have greater effects than NO\(_3^-\).
5. Thermodynamic studies showed that Cu(II) adsorption was an endothermic and spontaneous process. These experimental data and conclusions can provide support for the management of acidic mineral water discharge and the application of agricultural fertilizers in coal mining areas.

### Declarations

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Figures
Figure 1

Location of the sampling site. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

X-ray diffraction patterns
Figure 3

FT-IR spectrum

Figure 4

SEM with EDS analysis of the bulk soil (a, b) and clay fraction (c, d)
Figure 5

Effect of removal specific components of bulk soil(a) and clay fraction(b) on Cu(Ⅰ) adsorption: C0:CuⅠ: (10–200 mg/L), pH = 5.28±0.2, m/V = 5 g/L, I = 0.01 M NaNO3, t=24 h, T = 298.15 K.

Figure 6

Effect of initial pH on Cu(Ⅰ) adsorption: m/V = 50 g/L, C0(Cu): 30 mg/L, T = 298.15 K, I = 0.01 M NaNO3, and t=24 h

Figure 7
Effect of ionic strength on Cu($^{II}$) adsorption: C$_0$(Cu): (10–200 mg/L), m/V = 50 g/L, t=24 h, I = 0.01 M NaNO$_3$, pH = 5.28+0.2, and T = 298.15 K.

Figure 8

Effect of foreign ions on Cu($^{II}$) adsorption: C$_0$(Cu) = 10–200 mg/L, m/V = 50 g/L, I = 0.01 M NaNO$_3$, T = 298.15 K, pH = 5.28 + 0.2, and t = 24 h.

Figure 9

Linear plot of ln$K_d$ vs. 1/T of Cu($^{II}$) adsorption: C$_0$(Cu) = 50, 100 mg/L, I = 0.01 M NaNO$_3$, pH = 5.28 +0.2, m/V = 50 g/L, and t = 24 h.