

Research Article

An Experimental Study on the Adsorption and Desorption of Cu(II) in Silty Clay

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Heavy metals such as Cu(II) are widespread in the environment, and the impact of heavy metals on the environment of soils depends on the ability of soils to immobilize these pollutants. It is necessary to investigate the mechanism of interaction between heavy metal and soil from a soil remediation perspective. In this study, a series of experiments were conducted to investigate the adsorption and desorption behavior of Cu(II) in silty clay. Several impact factors such as pH, organic matter, temperature, and coexisted ions Zn(II) were considered. It was found that the adsorption process reached equilibrium after 4 hours of the experiment, and the data can be fitted well by the Elovich model and the double-constant model for the kinetic sorption process. The isothermal adsorption results showed that the adsorption rate reached a peak value when the initial concentration was about 20 mg L^{-1} . The decrease of H^+ can increase the adsorption activity of Cu(II) and reduce the ability of the desorption of Cu(II) ions. The adsorption capacity of Cu(II) is less than the desorption capacity under the condition of strong acidity and low concentration of Cu(II). In addition, the adsorption capacity of the native soil on Cu(II) was larger than that of the soil with the removal of organic matter, while the opposite was true for the desorption capacity on Cu(II). The maximum adsorption of Cu(II) occurred at 35°C for this study, and the binding energy increased as the temperature increased. Thermodynamic analysis revealed that the adsorption process of Cu(II) was spontaneous and endothermic. The Freundlich, Langmuir, Temkin, and Henry adsorption models were used for analyzing the adsorption isotherm of Cu(II), and it was found that the Freundlich model agreed the best with the experimental data compared with other three models. The results of the competitive adsorption experiments indicated that the competitive capacity of Cu(II) was greater than that of Zn(II) in low-permeability media such as silty clay, and the existence of binary metals can weaken the adsorption force between the single metal and the soil surface.

1. Introduction

Many industrial activities such as metal plating, mining operation, industry fertilizer, metallurgy, manufacturing battery, and dyeing in textile industries introduce heavy metals into the environment via their waste effluents [1]. A great deal of heavy metal ions from anthropogenic sources has been one of the most significant environmental problems because of their toxicity, persistence, and nonbiodegradable nature.

Cu(II), as one of the most widely used heavy metals in the industry, is considered a micronutrient but is extremely toxic to the living organism under relatively high concentrations [2, 3]. To reduce the harm caused by heavy metals to soil and plants, the European Union has established maximum

heavy metal limits for soil and for industry by-products such as biosolids and composts to be applied to fields. The soil criteria for Cu(II) set by the European Union is 140 mg kg^{-1} [4]. Hence, removal of Cu(II) from the soil and groundwater has been the subject of many studies [5–11].

Clay is a typical highly weathered soil. It is widely distributed all over the world and contains a great amount of Al and Mg oxides. Such soils have strong physical and chemical adsorption capacity, due to the soil particles with the large surface area, and carry a negative charge. In addition, different from other high permeability media such as sand, the unique mineralogy of clay such as porosity, pore size, and pore structure must be taken into consideration when studying clay's adsorbability. Several previous studies have focused

TABLE 1: Physical and chemical properties of the tested soil.

Sample	Grain components			CEC cmol kg ⁻¹	Organic matter g kg ⁻¹	pH	Cu(II) mg kg ⁻¹
	Clay particle ≤0.005	Silty grain 0.005–0.075	Sand grain 0.075–2				
	23.4%	63.14%	13.44%	5.83	20.46	5.57	2.904

TABLE 2: Mineral composition of the tested soil.

Quart (%)	Feldspar (%)	Calcite (%)	Dolomite (%)	Montmorillonite (%)	Chlorite (%)	Illite (%)	Kaolinite (%)
48	8	0	2	0	21	21	0

on the adsorbability of clay. For instance, Tassanapayak et al. [12] investigated the efficiency of clay in heavy ion sorption and found that it can be utilized as potential heavy metal adsorbents in wastewater treatment. Hasine et al. [13] also studied the role of clay properties in heavy metal ion sorption and desorption with a series of experiments and found that soil composition would greatly affect the sorption efficiency. Li et al. [14] pointed out that once the clay is contaminated, it is very difficult and it will take a very long time to remove the pollutants.

Adsorption is usually a primary process for the accumulation of heavy metals in soils while desorption is a main process for the removal. The study of adsorption and desorption processes is of utmost importance for understanding how heavy metals are transferred between the aqueous phase and the solid phase. Heavy metals in soils can be adsorbed as compounds like ions and complexes or exchangeable forms [15]. The most important interfaces involved in heavy metal adsorption in soils are predominantly inorganic colloids [16]. Heavy metal such as Cu(II) can be adsorbed into the soil and desorbed under certain conditions [17]. The mobility of heavy metals is often affected by the characteristics of soil, such as pH, amount of organic matter, temperature, and the types of ions.

Chenchao mining area is a famous iron mine, which is located in the central south of China (E'Zhou city, Hubei province). Cu(II) and Zn(II) are the two main toxic heavy metals in this mine. The surface soil in that area is mainly silty clay. In recent years, Cu(II) contamination to the soil has become an increasing concern there. In order to avoid continuous contamination on the soil and remediate the soil contaminated with Cu(II), it is necessary to investigate the adsorption-desorption behavior of Cu(II). Therefore, a series of experiments were conducted to understand how are the impacts of pH, amount of organic matter, and temperature on Cu(II) adsorption and desorption in single-metal solutions. The adsorption isotherm for Cu(II) in its aqueous solution will also be investigated to explore the mechanism of metal binding to adsorbent. Furthermore, we will investigate competitive adsorption onto the silty clay for solutions containing binary-metal mixtures of Zn(II) and Cu(II), which coexist in Chenchao mining area. The results of this study will provide some theoretical insights for preventing contamination and remediation of the contaminated soil.

2. Materials and Methods

2.1. Adsorbent. The soil samples, without contamination from heavy metals, were selected from the mining area. The soil samples were air-dried, then passed through a 60-mesh sieve. Some basic physicochemical properties of the samples are listed in Table 1, which shows that the soil can be classified as silty clay according to the People's Republic of China national standards GB/T50123-1999 "Earthwork Experimental Technique Standard". Mineral composition of soil samples is given in Table 2.

2.2. Instrumentation. The Cu(II) concentration in the solution was tested by UV-Visible spectrophotometer (Jasco-V-630, Japan) at a wavelength of 805 nm, and the pH was tested by HQ40d HACH pH (HACH company, USA). A thermostated rotary shaker (NRY-200, China) was used in all adsorption/desorption experiments.

2.3. Chemicals. Cu(NO₃)₂ and Zn(NO₃)₂ were used in adsorption/desorption experiments. The pH was adjusted by using 0.1 mol L⁻¹ HNO₃ or 0.1 mol L⁻¹ NaOH. The deionized water was used in the experiments.

2.4. Experiment Procedure. Experiments for the adsorption of Cu(II) in silty clay soil were carried out in a batch of tubes. The Cu(II) solutions were prepared by dissolving Cu(NO₃)₂ in deionized water and diluted to the required initial concentration (20 mg L⁻¹). In this study, the impact of several factors such as pH, organic matter, and coexisting ions on the adsorption and desorption of Cu(II) in the silty clay was examined.

For the kinetic adsorption experiments, 20 mL of Cu(II) solution (20 mg L⁻¹) was put in a 50 mL centrifuge tube with a fixed soil adsorbent dosage (1 g) and was agitated in a thermostated rotary shaker at a speed of 180 rpm at 25°C; the pH value of Cu(II) solution was set to be 5.5. At various time intervals, the adsorbent was separated from the samples by filtering and the filtrate was analyzed using a UV-Visible spectrophotometer.

For the adsorption isotherm experiments, different initial Cu(II) concentrations (0.5–200 mg L⁻¹) were agitated with 1 g soil adsorbent in a thermostated rotary shaker at the speed of 180 rpm for 24 hours. The pH value of Cu(II) solution was set to be 5.5. The adsorbent was separated, and the

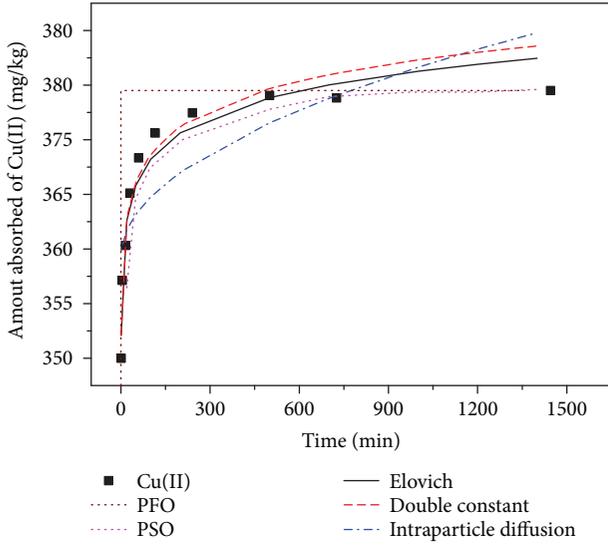


FIGURE 1: Kinetic adsorption models of Cu(II) on soil (conditions: pH 5.5, 60-mesh sieve particle size, 1 g adsorbent dosage, 180 rpm, and 25°C).

adsorbed Cu(II) was determined. The amount of adsorption q (mg kg^{-1}) can be calculated as

$$q = \frac{(C_{\text{init}} - C_{\text{eq}}) * V}{M * 1000}, \quad (1)$$

where C_{init} and C_{eq} are the initial concentration and equilibrium concentration of Cu(II), respectively (mg L^{-1}), V is the volume of aqueous phase (mL), and M (g) is the mass of soil. The percentage of adsorption (%) can be calculated using the following equation:

$$\text{Ads. (\%)} = \frac{C_{\text{init}} - C_{\text{eq}}}{C_{\text{init}}} \times 100. \quad (2)$$

For the desorption experiments, 20 mL NaNO_3 solution (0.01 mol L^{-1} , pH = 5.5) was put in the filtered residue of soil after the adsorption experiment and was agitated in the thermostated rotary shaker at a speed of 180 rpm for 24 hours. After that, taking the supernatant in the tube and measuring the Cu(II) concentration of the supernatant, the amount of desorption of Cu(II) can be obtained.

3. Results and Discussions

3.1. Kinetics of Adsorption. The results of kinetic adsorption of Cu(II) are presented in Figure 1. As shown in this figure, the adsorption process can be classified into two stages: a rapid adsorption at the early stage and a slow adsorption after a short period of time (around 4 hours). After 4 hours of the experiment, the amount of adsorption increases very slowly. This feature can be explained as follows: firstly, the quantity of vacant adsorption sites will decrease as time increases. Secondly, at the rapid adsorption stage, adsorption of Cu(II) mainly occurs on surfaces of soil particles or large pores. As time increases, adsorption of Cu(II) will occur on surfaces of inner small pores. Meanwhile, a stable complex or chelate

will form. Consequently, it will lead to a slow adsorption rate of Cu(II), which will approach an asymptote when time is long enough.

The following kinetic models are used to evaluate the mechanism of the adsorption process. These are the Elovich model, intraparticle diffusion model, double-constant model, pseudo-first order (PFO) kinetic model, and pseudo-second order (PSO) kinetic model. A brief introduction of these five models can be found in Appendix A. The fitting results of these five models are shown in Table 3 and Figure 1. One can see that both of the Elovich model and the double-constant model agree well with the experimental data, suggesting that these two models can describe the kinetic adsorption of Cu(II) in silty clay. The coefficient of determination (R^2) for the Elovich model and the double-constant model are very close to each (0.955 and 0.952, resp.). The applicability of the Elovich model and the double-constant model indicates that the adsorption kinetics experiment is a heterogeneous diffusion process. In addition, the good agreement with the Elovich model indicates the activation energy varies greatly during the sorption process.

3.2. Isothermal Adsorption. The results of the isothermal adsorption are shown in Figure 2(a). One can see that when the equilibrium concentration of the solution is low, the adsorption of Cu(II) increases rapidly. Similarly, we also observe that the adsorptive rate of Cu(II) increases rapidly at the beginning stage and then decreases gradually (Figure 2(b)). Specifically, the adsorption rate reaches a peak value when the initial concentration is about 20 mg L^{-1} . This phenomenon might be due to the chemical characteristics of Cu(II) and the number of the adsorption site of silty clay. Adsorption can be divided into two types according to the nature of heavy metals after being adsorbed, specific adsorption means that the soil organic matter or surface functional group forms stable metal chelate complexes; the metal ions fixed by specific adsorption can be desorbed only by strong acid and elements that have similar chemical properties or affinity. Nonspecific adsorption forms weak covalent bonds and outer complexes through electrostatic force and thermodynamic equilibrium [18].

When the initial concentration of Cu(II) is low, there are many adsorption sites on the soil surface, so most Cu(II) can be combined with high energy adsorption sites [19]. Therefore, specific adsorption accounts for a higher proportion, and the corresponding growth rate of adsorption is relatively high. As the equilibrium concentration increases, more Cu(II) joins the competition to take up sites. When the adsorption sites with a high binding energy approach the full capacity, the proportion of nonspecific adsorption increases. Cu(II) gradually reaches the adsorption equilibrium, and the rate of adsorption decreases subsequently.

In order to calculate the saturated adsorption capacity (Q_{max}) and the parameters related to adsorption capacity, four kinds of isotherms including the Freundlich, Langmuir, Temkin, and Henry models are used to analyze the adsorption of Cu(II). The details of these four models can be found in Appendix B. The fitting curves with the experimental data are shown in Figure 2(a), and the estimated parameters of

TABLE 3: Fitting parameters of kinetic models to Cu(II) adsorption.

Ion	The Elovich model $q_t = K_0 \ln t + C_0$			The intraparticle diffusion model $q_t = C_1 + K_1 t^{1/2}$			The double-constant model $\ln q_t = K_2 \ln t + C_2$			The PFO kinetic model $\ln(q_e - q_t) = \ln q_e - K_3 t$			The PSO kinetic model $t/q_t = 1/(q_e^2 K_4) + t/q_e$		
	C_0	K_0	r^2	C_1	K_1	r^2	C_2	K_2	r^2	q_e	K_3	r^2	q_e	K_4	r^2
Cu(II)	352.1	3.5	0.955	359.3	0.548	0.593	5.864	0.01	0.952	374.5	2.711	0.78	373	1.28	0.811

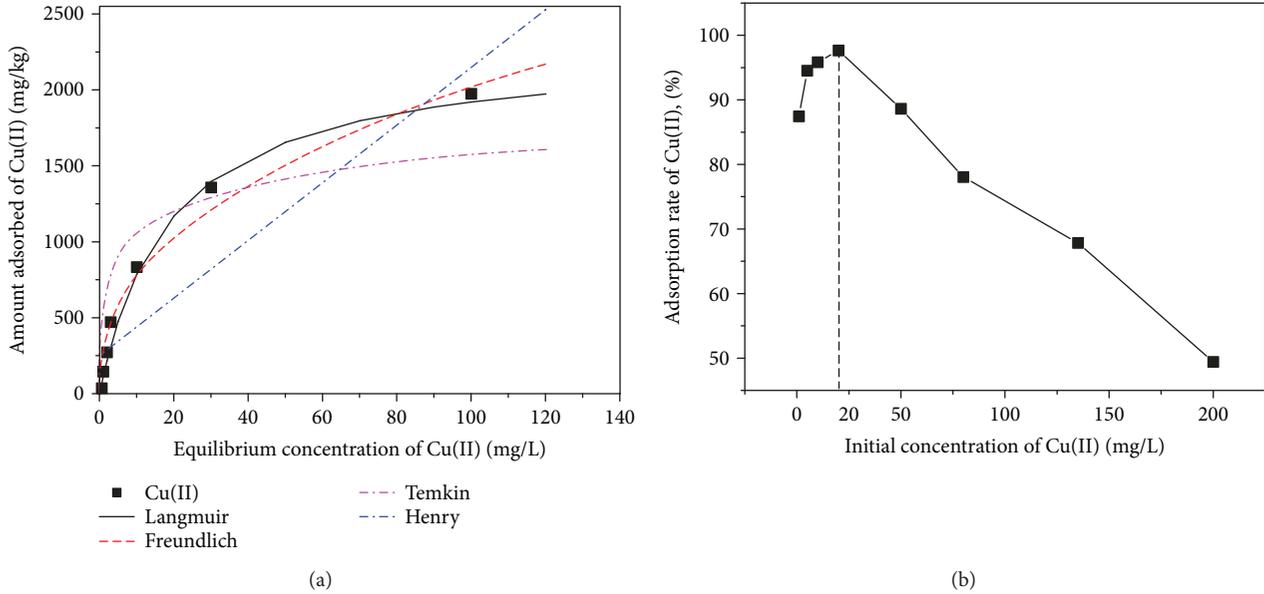


FIGURE 2: Adsorption isotherm of Cu(II): (a) adsorbed amount of Cu(II) and (b) adsorption rate of Cu(II).

adsorption isotherms are listed in Table 4. It is shown that the Freundlich model agrees the best with the experimental data, suggesting that Cu(II) adsorption onto silty clay is dominated by multilayer and heterogeneous adsorption.

In the following, we will investigate the influences of pH, organic matter, and temperature on the adsorption/desorption processes.

3.2.1. Effect of pH on Adsorption. In order to investigate the effect of pH on the isothermal adsorption, several experiments are conducted at different pH values of 2.0, 3.0, 4.0, and 5.5. The impact of pH on the adsorption of Cu(II) is shown in Figure 3. It is found that the sorption of Cu(II) increases as the pH increases (Figure 3(a)). This feature can be understood from a few aspects. Firstly, for the concentration with a low pH, the content of H^+ is high, which will lead to soil mineral dissolution, releasing ions such as Mg(II), Fe(II), and Al (III) [20]. These ions compete with Cu(II) for adsorption sites. Secondly, if the pH is low, the surface groups are protonated. Consequently, it will produce a positive surface charge which may weaken the ability to form complexes with Cu(II) [21]. Thirdly, with elevated pH, the ionic state may change, and the hydroxylation of Cu(II) makes Cu(II) more favorable to the soil.

It is also interesting to see that when pH is less than 4, with the increase of pH value, the soil adsorption rate of Cu(II) increases significantly (Figure 3(b)). When pH is

greater than 4, the adsorption rate of Cu(II) tends to be stable. This phenomenon may be related to the change of point-of-zero charge of soil, which is mainly controlled by pH. When the solution pH is less than the value corresponding to the point-of-zero charge, H^+ makes the surface of soil particles carrying positive charges; then soil adsorption sites decrease, leading to a low Cu(II) adsorption rate. With elevated pH, the content of H^+ decreases, leading to a large number of the hydroxyl group bond with soil particle; thus, the rate of adsorption increases. After the negative charge groups of soil surface reach equilibrium with Cu(II), the rate of adsorption will not increase anymore. Besides, when pH=2, a value much less than the point-of-zero charge (which is around 4 in this experiment), the adsorption rate can still reach 60%. It is shown that the adsorption rate is not only related to the soil charge but also influenced by the composition and properties of soil. Similar results have also been reported by Agbenin and Atin [21].

3.2.2. Effect of Organic Matter on Adsorption. The organic matter might have a great impact on adsorption [22]. Adsorption experiments are conducted using soil samples treated by 30% H_2O_2 to investigate the effect of organic matter on the adsorption of Cu(II) in silty clay. For this effort, initial Cu(II) concentration is set to be 0.5–200 $mg L^{-1}$, soil dosage is 1g, and pH is equal to 5.5. The adsorption results are shown in Figure 4. With the decrease of organic matter,

TABLE 4: Adsorption isotherm model parameters and coefficient of determination (R^2) for adsorption of Cu(II) at different conditions.

Parameters	Langmuir isotherm			Freundlich isotherm			Temkin isotherm			Henry isotherm		
	K ($L\ kg^{-1}$)	Q_{max} ($mg\ kg^{-1}$)	R^2	K_F ($mg\ kg^{-1}$)	n	R^2	A	B	R^2	K_p ($L\ kg^{-1}$)	D ($mg\ kg^{-1}$)	R^2
<i>pH</i>												
2.0	0.0124	1698.06	0.992	68.0	1.763	0.988	185.30	-67.99	0.825	7.79	75.9	0.909
3.0	0.0201	1747.64	0.997	91.6	1.831	0.989	169.05	132.49	0.776	9.61	128.3	0.888
4.0	0.0522	2027.98	0.968	262.3	2.411	0.997	188.73	503.40	0.838	16.14	228.8	0.840
5.5	0.0524	2286.39	0.971	304.4	2.440	0.990	217.60	-192.11	0.869	18.99	250.4	0.820
<i>C₀</i>												
Native soil	0.0524	2286.39	0.971	304.4	2.440	0.990	217.60	565.60	0.869	18.99	250.4	0.820
Reduce organic matter	0.0187	2129.93	0.976	99.82	1.597	0.932	323.58	-83.01	0.800	16.81	132.7	0.840
<i>T (°C)</i>												
10	0.0651	2053.32	0.972	311.3	2.269	0.993	196.88	561.95	2.569	16.95	254.9	0.798
25	0.0524	2286.39	0.971	304.4	2.447	0.990	217.60	565.60	0.869	18.99	250.4	0.820
35	0.2386	2840.71	0.958	417.8	2.905	0.965	234.58	639.45	0.928	18.48	302.6	0.743
<i>Solution composition</i>												
Single-metal solution	0.0524	2286.39	0.971	304.4	2.440	0.990	217.60	565.60	0.869	18.99	250.4	0.820
Binary-metal solution	0.0323	1882.17	0.971	191.8	2.300	0.982	167.17	372.10	0.774	11.52	243.3	0.827

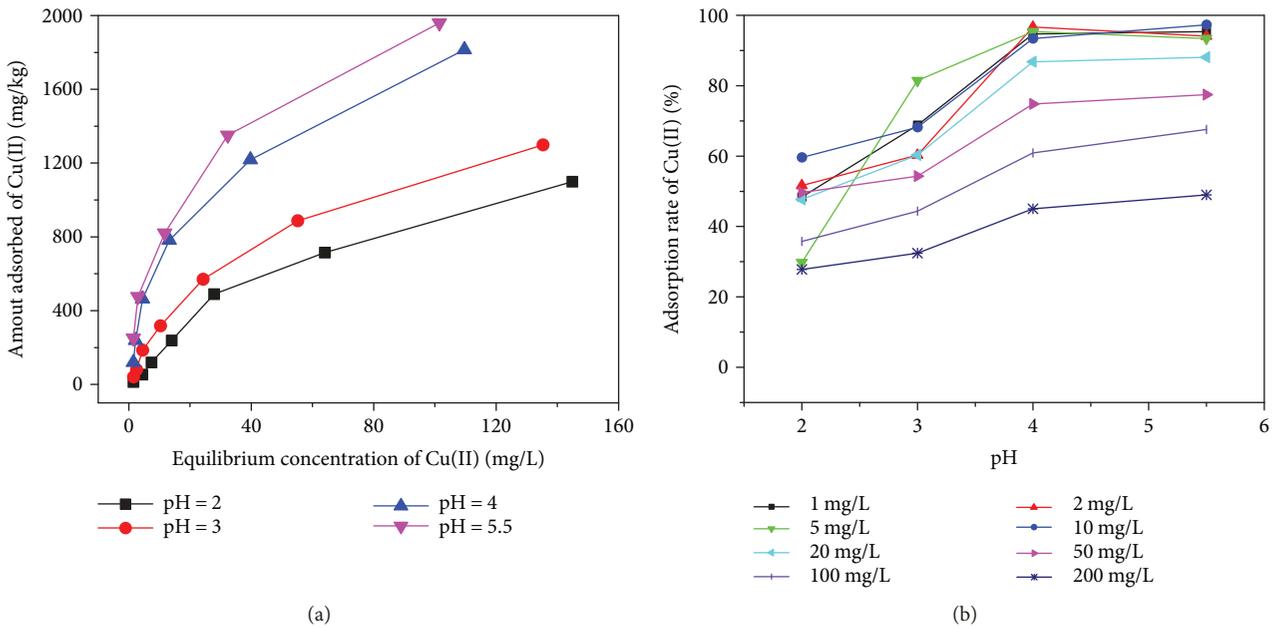


FIGURE 3: Effect of pH on adsorption: (a) adsorbed amount of Cu(II) and (b) adsorption rate of Cu(II).

the adsorption amount versus equilibrium concentration curve is the same as that of the untreated native soil, but the adsorption amount of Cu(II) is less than that of the native soil, given the same equilibrium concentration (Figure 4(a)). When the initial concentration of Cu(II) is relatively low (such as $0.5\ mg\ L^{-1}$), the adsorption amount and rate of the processed soil are much less than those of the native soil and they may even become negative (Figure 4(b)). This is because H_2O_2 may change the structure of soil particles, which will increase the mobility of Cu(II) in the original organic matter, and the original Cu(II) consequently

desorbs. Therefore, the amount of adsorption is less than that of desorption.

In addition, humic acid (HA) and fulvic acid (FA) are the two main components of soil; these components contain strong binding groups with heavy metals. The groups provide high energy sites for specific adsorption of Cu(II) on soil [18, 23]. In general, these sites can be easily combined with Cu(II) and form stable complexes. The H_2O_2 treatment has damaged the native layer structure and changes the surface properties. Under acid condition, H_2O_2 can promote degradation and diffusion of clay minerals, so the high energy sites of

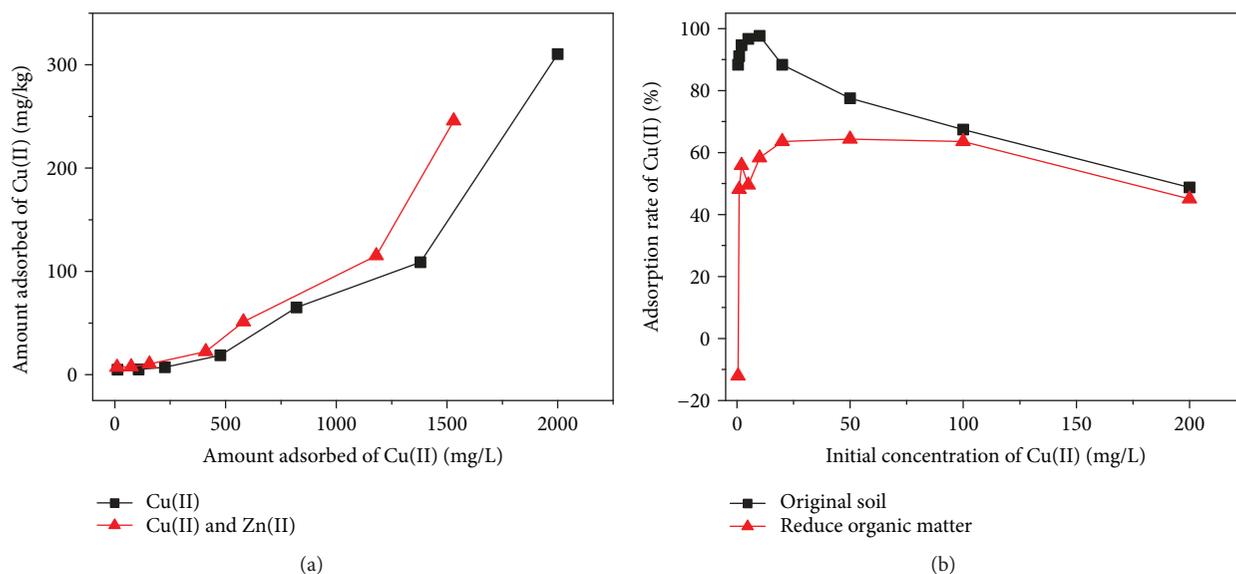


FIGURE 4: Effect of organic matter on adsorption: (a) adsorbed amount of Cu(II) and (b) adsorption rate of Cu(II).

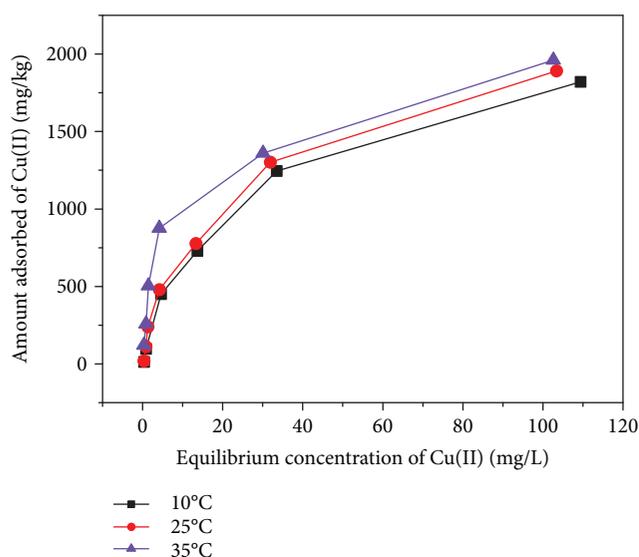


FIGURE 5: Effect of temperature on adsorption.

processed soil reduce rapidly, resulting in decreased specific adsorption. At low equilibrium concentration, adsorption of Cu(II) is dominated by specific adsorption, and the amount and rate of adsorption decrease as well. Similar results have also been found by Meyers and Quinn [24].

3.2.3. Effect of Temperature on Adsorption. Adsorption experiments are also conducted at three different temperatures of 10°C, 25°C, and 35°C, to investigate the effect of temperature, with initial Cu(II) concentration of 0.5–200 mgL⁻¹ and soil dosage of 1 g with pH=5.5. It is observed that the adsorption increases with the increase of temperature as shown in Figure 5. This is because that the adsorption energy of Cu(II) increases as the temperature increases, which

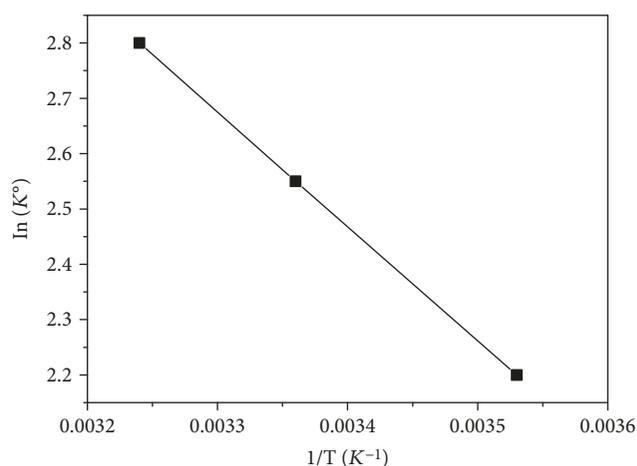


FIGURE 6: Thermodynamic parameters fitting curve of $\ln(K^\circ)$ versus $1/T$.

TABLE 5: Thermodynamic parameters for the adsorption of Cu(II) in aqueous onto clay.

T (K)	K°	ΔG° (KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
283.15	9.38	-5.27		
298.15	15.00	-6.71	19.58	87.85
308.15	18.26	-7.44		

makes Cu(II) easier to contact with sites; then it will improve the adsorption efficiency of Cu(II). In addition, the rise of temperature may change the properties of soil, such as pore size, and carbon activity.

To evaluate the metal ion-adsorbent system, thermodynamic parameters such as change in free energy (ΔG°),

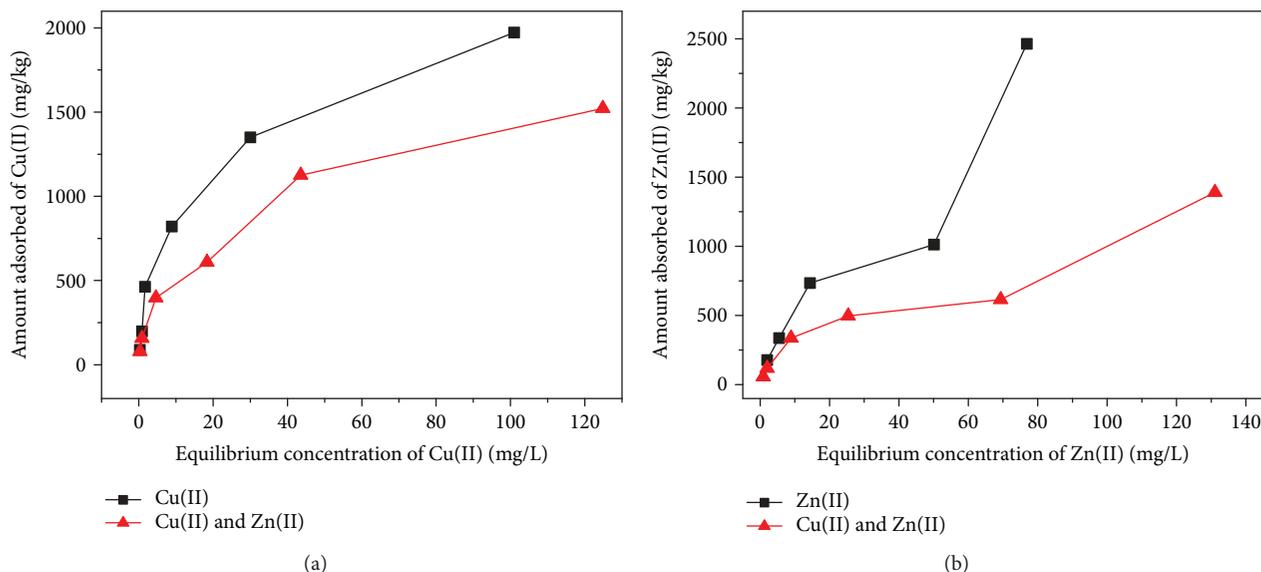


FIGURE 7: Adsorption in single-metal solution and the binary-metal solution: (a) adsorbed amount of Cu(II) and (b) adsorbed amount of Zn(II).

enthalpy (ΔH°), and entropy (ΔS°) are relevant and can be calculated by the following equations:

$$\Delta G^\circ = -RT \ln (K^\circ),$$

$$\ln (K^\circ) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}, \quad (3)$$

where R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature (K), and K° is the adsorption isotherm constant. ΔG° and ΔS° can be calculated from the slope and intercept of the plot of $\ln (K^\circ)$ versus $1/T$. The fitting curve is shown in Figure 6, and the results of thermodynamic parameters are shown in Table 5. Negative values of ΔG° and positive values of ΔS° indicate that the sorption of Cu(II) is spontaneous and endothermic. Therefore, it is no wonder to see that adsorption increases with the increase of temperature.

3.2.4. Effect of Competitive Adsorption of Cu(II) and Zn(II). It is also necessary to investigate adsorption when other ions coexist with Cu(II), as this is commonly seen in nature. Zn(II) is a common ion which can easily coexist with Cu(II) in many contaminated soil and groundwater systems. Therefore, we have conducted experiments to investigate the competitive adsorption of Cu(II) with the presence of Zn(II), and the results are shown in Figure 7. One can see from this figure that there is an obvious competition between Cu(II) and Zn(II), and the amount of adsorption in single-metal solution is much greater than that of the mixed binary-metal solution. The adsorption process can be divided into two stages for a mixed Cu(II) and Zn(II) solution. At a relatively low equilibrium concentration, there is a slight difference in the amount of adsorption between the single-metal and the binary-metal solutions. The difference increases gradually with the increase of equilibrium concentration. A possible reason is that adsorptions of Cu(II) and Zn(II) can be classified as specific adsorption at low equilibrium concentration. The competition is not obvious between two ions, as the sites could meet the demand

of adsorption for the two ions. When the sites approach the adsorption capacity as the initial concentration increases, the competitive adsorption becomes significant.

According to the decreased average adsorption rate shown in Figure 8, the average adsorption rate of Cu(II) is 86.69% when Zn(II) is not presented, while it is 73.08% when Zn(II) is presented, reflecting a 15.7% reduction (Figure 7(a)). The average adsorption rate of Zn(II) is 72.80% when Cu(II) is not presented, while it is 57.45% when Cu(II) is presented, showing a 21.1% reduction (Figure 7(b)).

In general, one can conclude that the competitive capacity of Cu(II) is greater than that of Zn(II). This phenomenon can be understood after the following considerations: firstly, the electronegativity of Cu(II) is greater than that of Zn(II), indicating greater ability of Cu(II) to adsorb electrons of ions. Secondly, the first-order hydrolysis constant of Cu(II) is greater than that of Zn(II); thus, the hydroxyl metal ions produced by hydrolysis are easily adsorbed by soil particles. Thirdly, the pliability parameter of Cu(II) is greater than that of Zn(II), which indicates a greater ability to form a covalent bond between soil colloid and metal ions.

3.3. Results of Desorption. Desorption experiments have also been conducted to evaluate the ability of soil to release heavy metal ions under certain conditions. Similar to the analysis of adsorption, the effects of pH, organic matter, temperature, and coexisted ions Zn(II) are examined.

3.3.1. Effect of pH on Desorption. Desorption experiments are carried out with pH of 2, 3, 4, and 5.5. The results show that the amount of desorbed Cu(II) decreases when pH increases, as shown in Figure 9(a). This phenomenon can be explained by considering the surface charge. The positive surface charge decreases with the increase of pH; thus, the combination of Cu(II) with soil becomes more stable. In addition, the influence of pH on the desorption rate is depicted in Figure 9(b). It is interesting to see that the average desorption

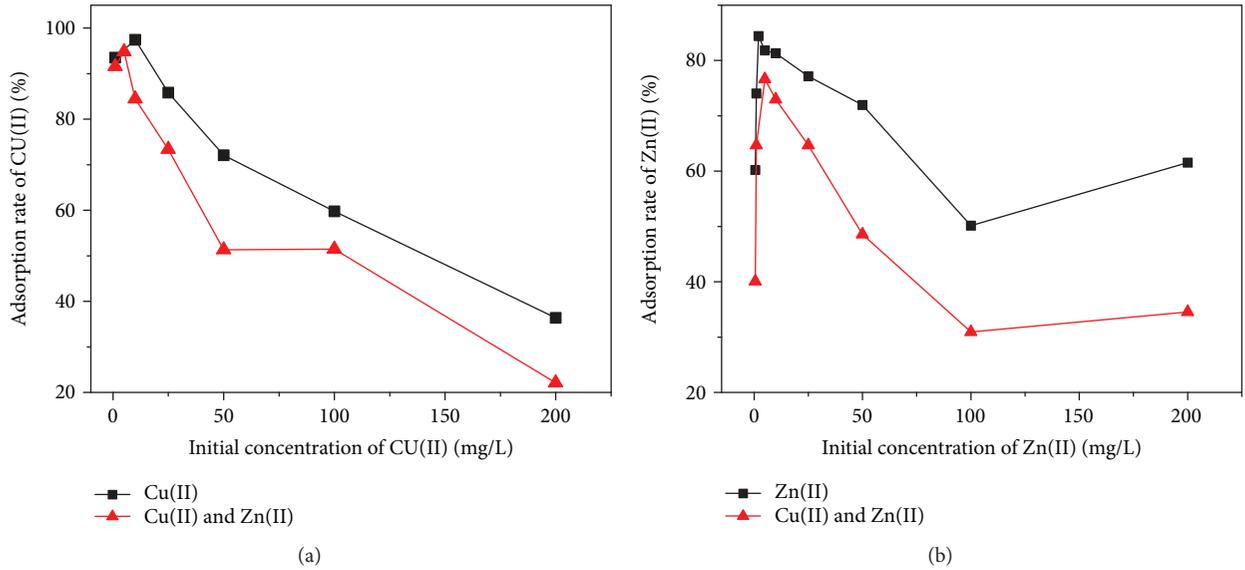


FIGURE 8: The adsorption rate of single-metal solution and binary-metal solution: (a) adsorption rate of Cu(II) and (b) adsorption rate of Zn(II).

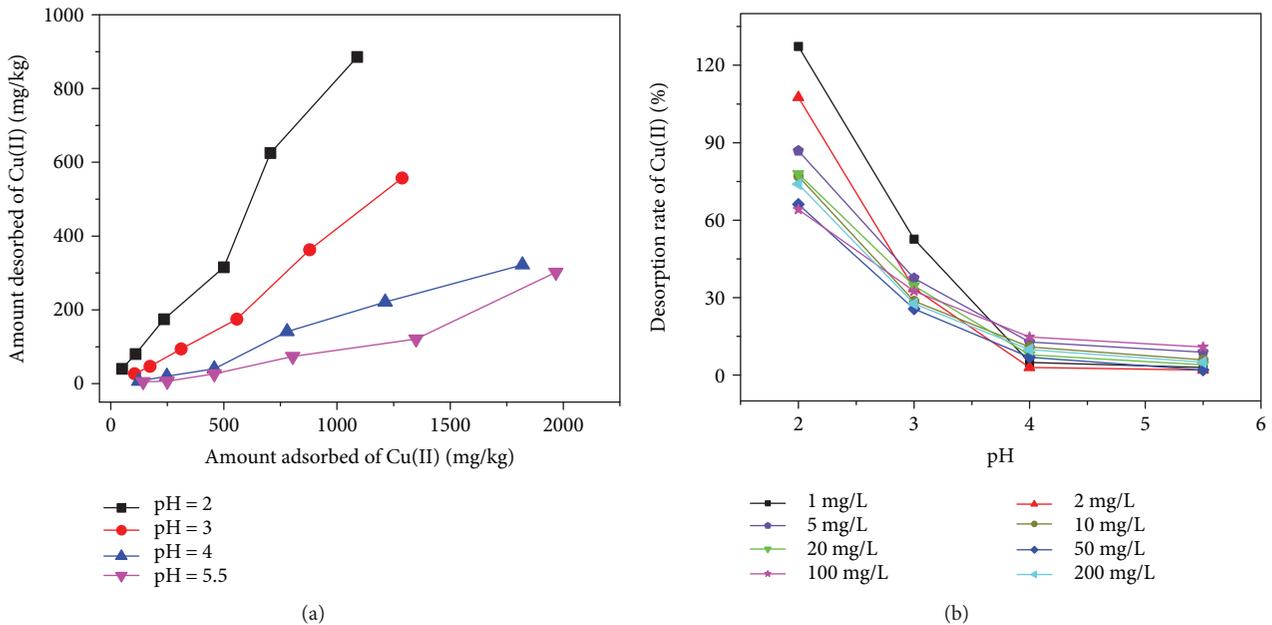


FIGURE 9: Effect of pH on desorption: (a) desorbed amount of Cu(II) and (b) desorption rate of Cu(II).

rate of Cu(II) is more than 100% at pH of 2; this implies that the background Cu(II), in addition to the adsorbed Cu(II), has been desorbed also because of a high concentration of H^+ at pH of 2. That is to say, the adsorption capacity of Cu(II) is less than the desorption capacity under strong acidity and low concentration of Cu(II).

3.3.2. Effect of the Organic Matter on Desorption. Desorption experiments are also conducted using soil samples treated by H_2O_2 to investigate the impact of organic matter on desorption. The results are shown in Figure 10. It is observed that the amount of desorption increases significantly after reducing organic matter. As discussed above, the proportion of

specific adsorption of Cu(II) decreases significantly as the organic matter decreases. On the contrary, the proportion of nonspecific adsorption is higher than that of the native soil. It is notable that it is easier to desorb for the nonspecific adsorption case than the specific adsorption case. Consequently, significant desorption of Cu(II) is found for treated soil, as shown in Figure 10.

3.3.3. Effect of Temperature on Desorption. Desorption experiments are also conducted at three different temperatures of $10^\circ C$, $25^\circ C$, and $35^\circ C$. As shown in Figure 11, the amounts of desorbed Cu(II) decreases as temperature increases. The effect of temperature can be explained by considering the

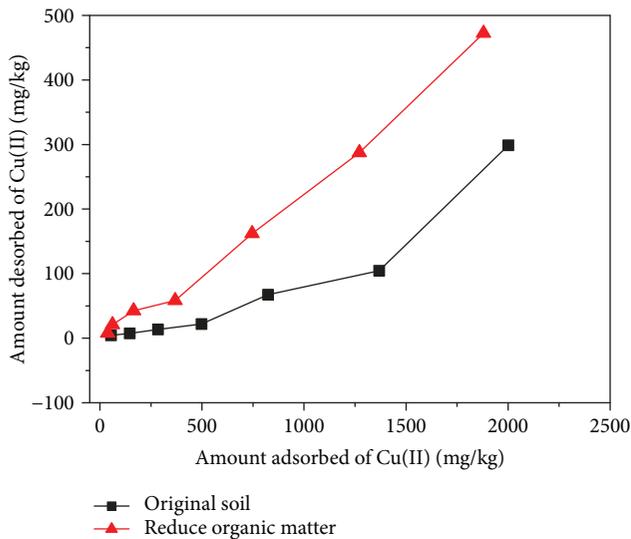


FIGURE 10: Effect of organic matter on desorption.

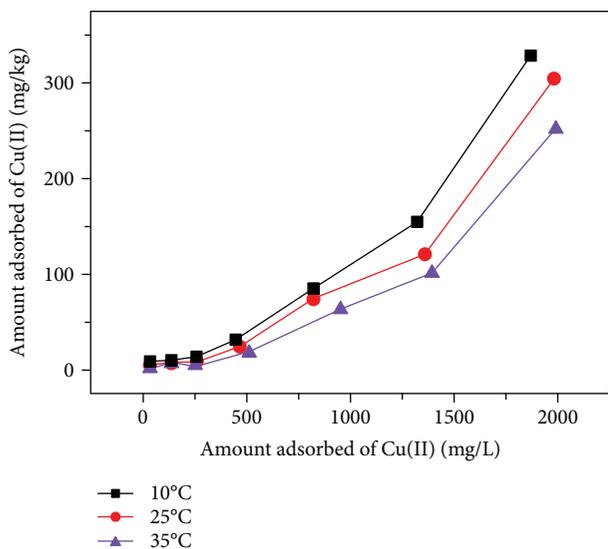


FIGURE 11: Effect of temperature on desorption.

binding energy of Cu(II). Since the binding of Cu(II) increases as the temperature increases, the combination of Cu(II) with soil at a relatively higher temperature is more stable than that at a lower temperature. This indicates that a higher temperature will result in a higher proportion of specific adsorption under the experimental conditions of this study.

3.3.4. Effect of Competitive Desorption of Cu(II) and Zn(II). Desorption experiments are carried out in coexisted Cu(II) and Zn(II) solutions to investigate the competitive desorption of Cu(II) and Zn(II). The amount of desorbed Cu(II) in the binary-metal solution of Cu(II) and Zn(II) is greater than that of the single-metal solution of either Cu(II) or Zn(II), as shown in Figure 12. This is because the competition between Cu(II) and Zn(II) will decrease the possibility of the two ions to attach with the high binding energy

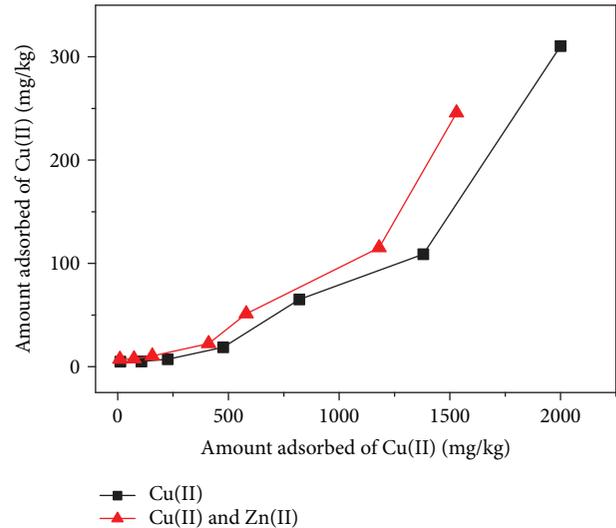


FIGURE 12: Desorption of Cu(II) in single-metal and binary-metal solutions.

adsorption sites. Consequently, the competitive adsorption is less stable for the binary-metal solution than that for the single-metal solution. Thus, it is easier to desorb Cu(II) for the case with Cu(II) and Zn(II) in the solution, as shown in Figure 12.

4. Conclusions

In this study, a series of experiments are carried out in a batch of tubes. Kinetic adsorption experiments are performed at 25°C, pH = 5.5; initial Cu(II) concentration is set to be 20 mgL⁻¹. Isothermal adsorption experiments are performed at 25°C, pH = 5.5, with different initial Cu(II) concentrations (from 0.5 to 200 mgL⁻¹). Several impact factors including pH, organic matter, temperature, and coexisted Zn(II) ions are considered. Desorption experiments are carried out under the same conditions using NaNO₃ solution (0.01 molL⁻¹). The main results obtained in this study can be summarized as follows:

- (1) The kinetic adsorption process can be divided into two stages: a rapid adsorption stage followed by a slow adsorption stage. The rapid uptake is mainly concentrated in the first 4 hours. The experimental data of the kinetic adsorption can be fitted well by the Elovich model and the double-constant model.
- (2) The isothermal adsorption results reveal that the adsorption rate reaches a peak value when the initial concentration is about 20 mgL⁻¹. The isothermal adsorption can be fitted well by the Freundlich model.
- (3) The pH value plays an important role in adsorption and desorption processes. The high concentration of H⁺ could improve the migration ability of exogenous Cu(II) in silty clay and reduce the strength of Cu(II) adsorption. In addition, the adsorption

capacity of Cu(II) is less than the desorption capacity under strong acidity and low concentration of Cu(II).

- (4) The organic matter is found to have a great impact on the soil particle adhered to metal ions. Specifically, the adsorption capacity of the native soil is larger than that of soil with the removal of organic matter, whereas the ability to desorb Cu(II) is opposite.
- (5) The kinetic energy of Cu(II) is higher at higher temperature. The calculated thermodynamic parameters reveal that the adsorption process of Cu(II) is spontaneous and endothermic.
- (6) The existence of binary metals weakens the adsorption force between the single metal and the soil surface. It is found that the competitive capacity of Cu(II) is greater than that of Zn(II).
- (7) The results show that the combination of Cu(II) and silty clay is relatively stable, and the migration and transformation of Cu(II) are difficult to occur under certain conditions (say, pH of 5.5, temperature of 35°C, organic-rich soil, and without other heavy metal ions).

Appendix

A. Kinetic (or Nonequilibrium) Sorption Models

The Elovich equation [25] is one of the most widely used equations for the kinetic adsorption of solute from an aqueous solution, which can be expressed as

$$\frac{dq_t}{dt} = \alpha e^{(-\beta q_t)}, \quad (\text{A.1})$$

where α is an initial adsorption rate ($\text{mg kg}^{-1} \text{ min}^{-1}$), β is a desorption constant (kg mg^{-1}), and q_t is the amount of Cu(II) adsorbed (mg kg^{-1}) on the adsorbent at time t . The Elovich model was developed on the basis of the diffusion, or the chemisorption is dominant for the sorption process. A simplified equation of A1 can be expressed as

$$q_t = K_0 \ln t + C_0, \quad (\text{A.2})$$

where K_0 and C_0 are two empirical constants to be determined from experimental data.

The intraparticle diffusion model [26, 27], derived from Fick's second law of diffusion, is used to analyze and elucidate the diffusion mechanism, and is expressed as

$$q_t = C_1 + K_1 t^{1/2}, \quad (\text{A.3})$$

where C_1 is an intercept constant indicating the effect of boundary layer to adsorption and K_1 is an intraparticle diffusion rate constant. Values of K_1 and C_1 are calculated from the plot of q_t against $t^{1/2}$.

The double-constant model [28] is suitable for heterogeneous diffusion process. It is given as

$$\ln q_t = C_2 - K_2 \ln t, \quad (\text{A.4})$$

where C_2 is an intercept constant and K_2 is an adsorption rate constant.

The pseudo-first order (PFO) kinetic model [29] provides a simplified description of often complicated kinetic-sorption mechanisms, which can be expressed as

$$\ln (q_e - q_t) = \ln q_e - K_3 t, \quad (\text{A.5})$$

where q_e (mg kg^{-1}) is the amount adsorbed at equilibrium and K_3 is a rate constant of the pseudo-first order kinetic model.

The pseudo-second order (PSO) kinetic model [30] is represented by

$$\frac{t}{q_t} = \frac{1}{q_e^2 K_4} - \frac{t}{q_e}, \quad (\text{A.6})$$

where K_4 is the pseudo-second order rate constant for sorption. For this model, the sorption process is controlled by chemisorption, and the sorption capacity is controlled by the number of the active sorption sites. This chemisorption mechanism involves the sharing of electrons or the transfer of electrons between adsorbates and adsorbents.

B. Isothermal (or Equilibrium) Sorption Models

The Freundlich model [31] is generally applied to describe sorption isotherm, which can be expressed as

$$W = K_F C^{1/n}, \quad (\text{B.1})$$

where W is the adsorbed amount of Cu(II) (mg kg^{-1}) and C is the concentration of Cu(II) (mg L^{-1}). K_F is a constant (mg kg^{-1}) indicative of efficiency of adsorption of ions and n is a constant indicative of the intensity of adsorption of ions.

The Langmuir model is commonly applied to the monolayer chemisorption of the gaseous phase, applicable to the aqueous phase under most circumstances. This isotherm is mainly applied when no strong adsorption is expected, and the adsorption surface is uniform [32]. A commonly used formula of the Langmuir adsorption isotherm is

$$\frac{C}{W} = \left(\frac{1}{K Q_{\max}} \right) + \left(\frac{1}{Q_{\max}} \right), \quad (\text{B.2})$$

where C and W are defined the same way as in (A.5), Q_{\max} is the saturated adsorption (or adsorption capacity) (mg kg^{-1}), and K is a constant (L Kg^{-1}), which reflects the bonding energy between solution and ions.

The Temkin model [33] is often used to describe the uneven surface of a soil particle, which can be expressed as

$$W = A \ln C + B, \quad (\text{B.3})$$

where A and B are two empirical constants.

The Henry model is a very simple linear form to describe adsorption and is defined as

$$W = K_p C + D, \quad (\text{B.4})$$

where K_p is an adsorption constant (L kg^{-1}) and D is the initial amount of adsorbed ions (mg kg^{-1}).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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