===== **SOIL CHEMISTRY** =====

Copper Sorption and Transport in an Acidic Brown Soil

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Abstract—The sorption and transport of copper (Cu) in an acidic brown soil were studied using batch and column experiments. The results showed that Cu adsorption fitted better Langmuir isotherm at low pH (3.13) whereas Freundlich equation fitted better at high pH (5.87), and affinity (K and K_{F}) increased significantly from 0.00676 to 0.0121 L mg^{-1}, and from 33.05 to 135.98, respectively, with pH increase, resulting in a very great increase in adsorption capacity ($Q_{\max}$) from 970 to 2272 mg kg^{-1}. Its kinetics was found to be better described by a pseudo-second order model ($R^2 > 0.997$), where sorption rate (k_2 and h) was as low as 0.0237 and 0.0013 kg mg^{-1} d^{-1}, and 23.89 and 106.12 mg kg^{-1} d^{-1}, respectively, at pH 3.19, much lower (10−20 times) than those at pH 6.92. At pH 5.87, the breakthrough curve of Cu showed substantial retardation and low peak concentration ($C/C_0 = 0.64$); whereas at pH 3.17, full breakthrough ($C/C_0 = 1$) was observed, meaning great increase in mobility of Cu. Generally, two different mechanisms governed Cu sorption and transport: CuOH$^+$ was precipitated on clay mineral surface and weaker complexation with DOM at higher pH (>5); whereas Cu^{2+} adsorbed to SOM surface and stronger complexation with DOM at lower pH (<4.2).

Keywords: Bordeaux mixture, adsorption capacity of soils

INTRODUCTION

Copper-based fungicides such as Bordeaux mixture ($CuSO_4 \cdot 5H_2O$ + Ca(OH)$_2$) are used to prevent fungal diseases on a variety of vineyard and orchard soils (apple, grape, pear, cherry, peach, etc.). Their long-term extensive use has led to accumulation and pollution of Cu in soils [17, 20, 29, 39, 55]. For example, Mirlean et al. [39] showed that Cu maximum value in Brazil's vineyard soils was much as 3200 mg kg^{-1}, several times higher than 100 mg kg^{-1}, threshold for soil contamination [17]. At high concentrations Cu is toxic to plants and microorganisms in soils, e.g., reducing the density of root hairs, decreasing photosynthesis, affecting nitrogen metabolism, especially reducing absorption of water and nutrients [9, 50, 57]. In addition, the losses were also expected with Cu accumulation above the adsorption capacity of soils, causing contamination of surface and subsurface waters.

Numerous studies have demonstrated that Cu mobility is mainly controlled by sorption to soil organic matter (SOM), where carboxylic and hydroxylic (or amine) groups form very stable five- to six-membered ring chelates with Cu^{2+} [11, 18, 21, 27, 35]. Cu can also adsorb to Fe-, Mn- or Al-(hydro)oxides, and clay minerals, forming inner-sphere complexes and/or surface precipitates [7, 8, 14, 46]. Such strong sorption made it one of the least mobile metals in soils. However, Sun et al. [50] showed that Cu has potential to leach from surface horizon into a lower horizon in extreme sandy soils with little SOM (<0.5%).

Shandong Peninsula of China is an important fruit-producing area, where brown soil is the dominant soil type, and strong acidification occurred after 40-year intensive cultivation, resulting in a 1.5 pH decrease from 6.8 to 5.3 [54]. More importantly, its SOM decreased linearly with soil acidification and was 2.3% for pH 6 and 0.74% for pH 4 [54]. Our investigation in Hunan, Jiangxi and Shandong also showed a high positive linear correlation between SOM and soil pH (data not shown). The low SOM content driven by soil acidification probably weakened Cu sorption and thus promoted its mobility. Some researches evidenced that dissolved organic matter (DOM) governed the mobilization of Cu due to Cu-DOM complexation [26, 58], and even Mehlhorn et al. [36] suggested the DOM : SOM ratios. The solubility of DOM is pH-dependent and significant increases in DOM have been observed when pH is raised [13, 40]. Obviously, there is a confliction in the descriptions for Cu mobility at lower pH where whether it increased due to a decrease in sorption capacity (releasing freer Cu (II) ions) or whether it decreased due to a decrease in DOM concentration (producing less DOM-Cu (II) complexes). Temminghoff et al. [52] showed that although DOM-Cu at low pH (3.9) was only about 1/3 of that at high pH (6.6), extractable Cu concentration

for the former was about 5 times larger than that for the latter, implying the increase in Cu mobility at low pH. Our previous study [60] evidenced that Cu sorption on soils is governed by pH-regulated surface adsorption followed by diffusion into the micropores of SOM and/or clay minerals, where surface precipitation or polymerization of $CuOH^+$ dominated at higher pH whereas at lower pH the micropore diffusion of Cu^{2+} made a considerable contribution to aging (decreasing its mobility). Therefore, the complex changes that occurred during soil acidification due to the different dominant sorption species and sorption mechanisms have led to great changes in Cu mobility that are difficult to predict.

In any events, it is crucial to understand Cu behavior and fate in acidified soils. In this study, the kinetics of sorption and transport of Cu in an acidic Cambisols under different pHs were investigated. The objectives were: (1) to quantify the influence of pH on the sorption rate and transport of Cu; and (2) to determine the fate and behavior of Cu in response to soil acidification.

OBJECTS AND METHODS

Soil sample. Surface soil (0−20 cm depth) under a pine forest at the foot of Phoenix Hill, Yantai, Shandong, China (121.44° E, 37.47° N), was collected in October 2012, air-dried, ground and passed through a 2 mm-sieve for batch and column experiments. Following the methods described by Lu [33], the soil basic properties were determined as follows: pH 5.87, organic matter (SOM) 2.84%, total Cu 14.0 mg kg^{-1}, and sand (2.00−0.05 mm) 67.0%, silt (0.05−0.002 mm) 31.1% and clay (<0.0002 mm) 1.9%. Briefly, the soil pH was determined using a pH meter (PHS-3C, Shanghai INESA Instruments Co., Ltd., Shanghai, China) in a soil/water ratio of 1 : 2.5 (V : V); SOM was measured by potassium dichromate oxidation titration; Total Cu content was determined by atomic absorption spectrophotometer (AAS) (ZEEnit 700, Analytik Jena AG, Germany) after triacid digestion (HNO_3-HClO_4-HF). Soil sand, silt and clay were measured using a laser particle analyzer (Malvern Mastersizer 2000F, Malvern Instruments Ltd., UK). This sandy acidic soil was classified as Cambisols (WRB 2014) [24].

Equilibrium batch experiments. H^+ would be released during Cu sorption, but the effect may be partly offset in some concentration of electrolyte in particular nitrate for constant charge soils [42, 61]. So, 0.005 M $Ca(NO_3)_2$ was used as supporting electrolyte in this study to keep ionic strength constant and maintain a more consistent matrix during sorption and transport of Cu.

Equilibrium batch experiments were conducted to obtain adsorption isotherms and adsorption edges of Cu in the soil [23, 49]. For adsorption isotherms, the experiments were initiated by mixing 3.0 g soil with 10 mL background solution [0.005 M $Ca(NO_3)_2$] in 50 mL centrifuge tubes. The pH of mixture was measured using pH-meter and adjusted repeatedly with 0.5 M $HNO_3/Ca(OH)_2$ to initial pH 3 or 6. Then 0.005 M $Ca(NO_3)_2$ solution was added until the total volume of supernatant solutions reached 20 mL. Finally, 10 mL Cu solutions [prepared in 0.005 M $Ca(NO_3)_2$] with wide range of initial concentrations (0.15 ~ 30 mM) were added and the centrifuge tubes were capped. For adsorption edges, the pH of mixture was adjusted to initial values of 3, 4, 5, 6, and 7, respectively, and followed by adding 10 mL 1.0 mM $Cu(NO_3)_2$ in 0.005 M $Ca(NO_3)_2$ solution (soil/water = 1/10).

All centrifugal tubes were continuously shaken in a constant temperature water bath shaker (HZS-H, Harbin Donglian Eelectronic and Technolgy Development Co., Ltd., Heilongjiang, China) at 25°C for 24 h followed by centrifuging at 4000 rpm min^{-1} for 15 min. The Cu concentration in supernatant solutions was analyzed using AAS. All treatments were conducted in triplicates.

Kinetic batch experiments. The time-dependent sorption of Cu in the soil was determined using kinetic batch experiments under various pHs. According to the same procedure mentioned above, the mixture (3 g soil + 30 mL solution) was adjusted to initial pH of 3, 5, and 7, respectively. The initial concentration of Cu [as $Cu(NO_3)_2$ prepared in 0.005 M $Ca(NO_3)_2$] were 0.15 mM and 1.5 mM, respectively. The centrifuge tubes were capped and incubated in a constant-temperature incubator (BPX-272, Boxun Medical Biological Instrument Corp., Shanghai, China) at 25°C for 1, 5, 10, 28, and 90 days, respectively. After the incubation, the supernatant solutions were centrifuged at 4000 rpm min^{-1} for 15 min and Cu concentrations were measured using AAS. All treatments were conducted in triplicates.

Column experiments. Miscible displacement column experiments as described by Elbana and Selim [15] were performed in an air-conditioner laboratory for maintaining constant temperature (25°C) during whole experiment process. Two acrylic columns (A and B) (10-cm in length and of 2.2 cm i.d.) were uniformly packed with air-dry soil, and the basic characteristics were given in Table 1. To ensure water saturation, upward flow in the soil columns was maintained. Constant flux was controlled by a peristaltic pump (BT 102S, Baoding Longer Precision Pump Co., Hebei, China). Effluents from columns were collected using an automatic fraction collector (CBS-A, Shanghai Huxi Analysis Instrument Factory Co., China) at regular time interval and analyzed by AAS.

Column A was initially saturated with a background solution of 0.005 M $Ca(NO_3)_2$ (pH 5.87). Following saturation, approximately 145 pore volumes of 10 mg L^{-1} Cu [in the form of $Cu(NO_3)_2$ in 0.005 M $Ca(NO_3)_2$] with pH of 5.87 was introduced into the column. After that, the column was leached with
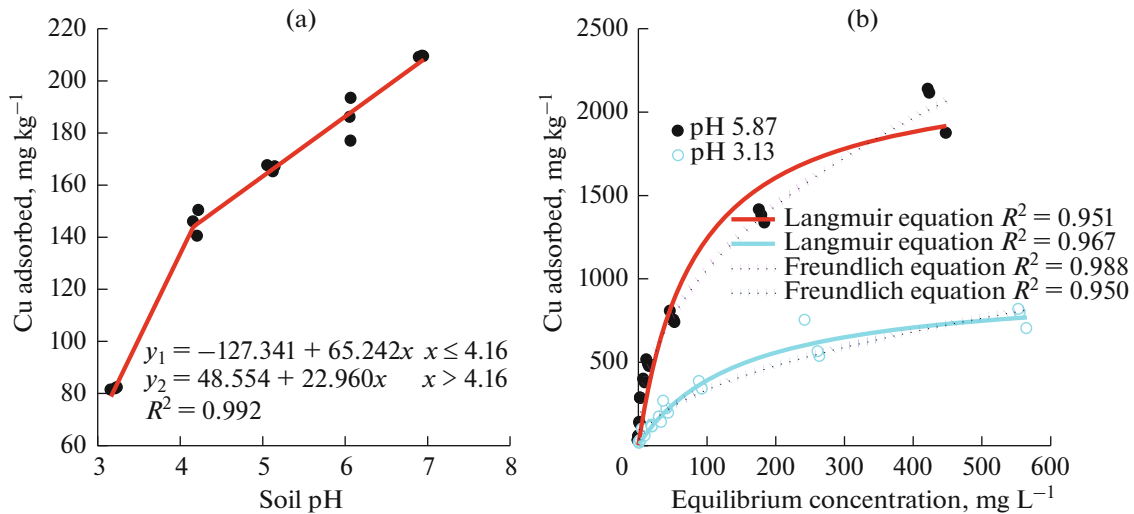
Fig. 1. (a) Effect of pH on Cu adsorption ($C_0 = 0.33$ mM); (b) Cu adsorption isotherms at pH 3.13 and 5.87.

about 102 pore volumes of 0.005 M Ca(NO$_3$)$_2$ with pH of 5.87. To measure the effect of soil acidification on copper release, column A was further leached with 0.005 M Ca(NO$_3$)$_2$ solution adjusted to pH 3.17.

Similarly, column B was initially saturated with 0.005 M Ca(NO$_3$)$_2$ adjusted to pH 3.17 followed by approximately 80 pore volumes of 10 mg L^{-1} Cu in 0.005 M Ca(NO$_3$)$_2$ (pH 3.17), and then leached with 0.005 M Ca(NO$_3$)$_2$ (pH 3.17).

RESULTS AND DISCUSSION

pH-dependent adsorption isotherms of Cu. Cu adsorption increased markedly from 81.5 to 209.2 mg kg^{-1} (38.5 to 98.8% of added Cu) with increase in pH from 3.2 to 6.9, yielding two linear segments with different slopes (Fig. 1a). One was 65.2 at pH < 4.2, and the other was 23.0 at pH > 4.2, which means that two adsorption mechanisms were possible with increase of soil pH: monolayer and multilayer adsorption at low coverages at low pH, and surface precipitation or surface polymerization at high coverages at high pH. Furthermore, Cu adsorption isotherms at low (3.13) and high (5.87) pH were shown in Fig. 1b and Table 2. Langmuir and Freundlich adsorption models displayed good fits ($R^2 = 0.950 \sim 0.988$), where affinity parameters related to the bonding energy (K and K_F) increased significantly from 0.00676 to 0.0121 L mg^{-1}, and from

33.05 to 135.98, respectively, with pH increase from 3.13 to 5.87, and thus causing a very great increase in adsorption capacity (Q_{max}) from 970 to 2272 mg kg^{-1}. Moreover, the decrease in Freundlich parameter b representing dimensionless heterogeneity [19] with pH, suggested that at lower pH (<4.2) Cu adsorption was possibly a homogeneous adsorption, whereas at higher pH (>4.2) nucleation and surface precipitation with non-uniform distribution of adsorption affinities over the heterogeneous surface might occur [3, 5, 19, 51].

In addition, Langmuir isotherm seems good for Cu adsorption at lower pH while Freundlich is better for its adsorption at higher pH, which also suggested that two adsorption mechanisms are at work: adsorption on homogeneous surfaces and followed by nucleation on heterogeneous surfaces. Lodygin [32] also showed possible existence of two fixation mechanisms of Cu ions on the surface of humic acid. In short, Cu adsorption on Cambisols was highly pH-dependent, resulting in lower adsorption at lower pH whereas higher nucleation/precipitation at higher pH. Generally, surface negative charge increases with increasing pH, causing marked increase in metal cation adsorption. More importantly, monovalent metal cation (MOH$^+$), which adsorbs more easily on soil surfaces than bivalent cation (M^{2+}), also increases with increase in pH, resulting in surface nucleation/precipitation of hydroxides of transition metals [6]. Surface clusters of Cu hydrox-

Table 1. Conditions of soil column displacement experiments

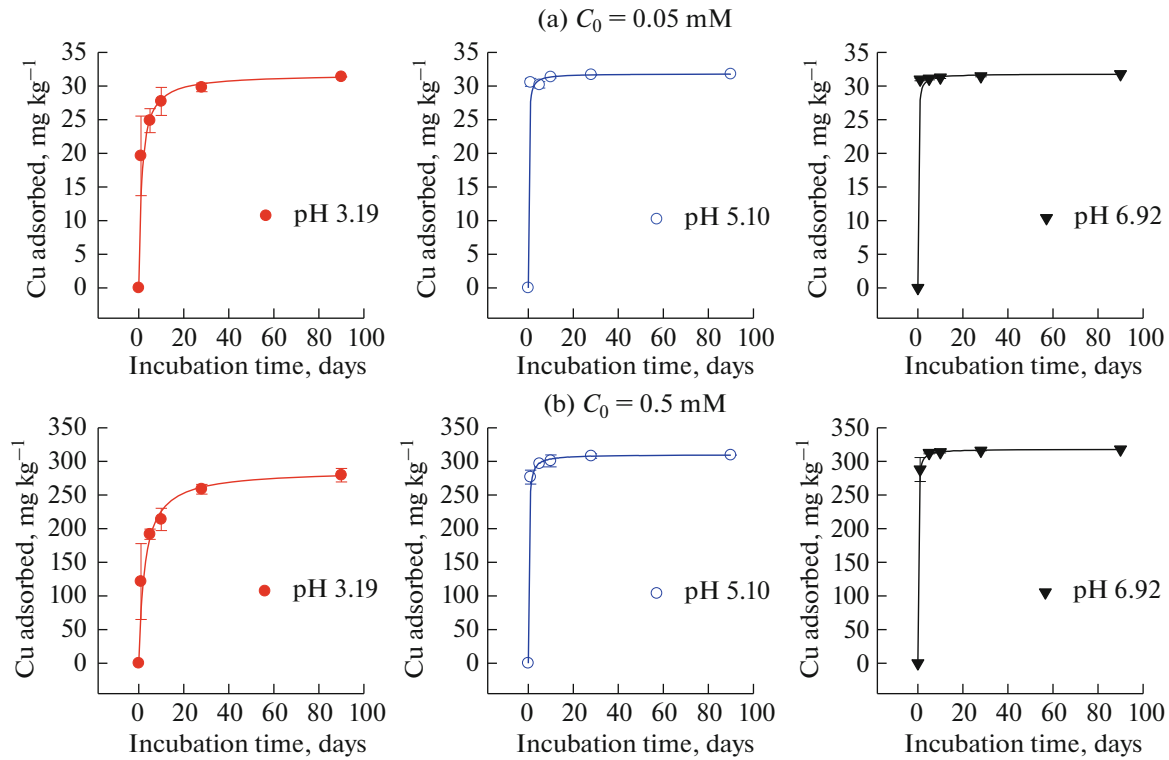| Column	pH	Bulk density, g cm^{-3}	Saturated water content, cm^3 cm^{-3}	Darcy velocity, cm min^{-1}	Average pore-water velocity, cm min^{-1}
A	5.87	0.99	0.627	0.0295	0.0470
B	3.17	1.03	0.611	0.0460	0.0753

Fig. 2. Effect of pH on Cu slow reaction (irreversible process) onto Cambisols ((a) $C_0 = 0.05$ mM; (b) $C_0 = 0.5$ mM).

ide and/or precipitates of $Cu(OH)_2$ can form at high pH (e.g., 7.5 and 5.6, respectively, for hydrous oxides of Fe and Al), which has been confirmed by spectra data [1, 10, 28].

Slow kinetics of Cu added to Cambisols. Cu sorption showed a pronounced aging effect, especially under lower pH and higher initial concentration, where Cu mobility and bioavailability declines continuously and slowly with time, lasting for several months or years (Fig. 2) [2, 31, 34, 45, 60]. For example, Arias-Estevez et al. [2] demonstrated that 500 days of incubation in an acidic soil were still inadequate for the aging of added Cu more than 500 mg kg^{-1}.

Various kinetic models such as Lagergren pseudo-first order, pseudo-second order, Elvoich, and intra-particle diffusion equation have been widely applied to describing ion reaction at the particle/solution interface [16, 47, 48]. Among them Lagregren pseudo-first order rate equation is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \qquad (1)$$

where q_e and q_t are the amount adsorbed (mg kg^{-1}) at equilibrium and at any time t (d); k_1 is the rate constant of Lagergren pseudo-first order model (d^{-1}).

Pseudo-second order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \qquad (2)$$

where k_2 is the rate constant of pseudo-second order model (kg mg^{-1} d^{-1}). The initial adsorption rate (mg kg^{-1} d^{-1}), h, of the second order process as $t \to 0$ is defined as:

$$h = k_2 q_e^2, \qquad (3)$$

Elovich equation is generally simplified as follows:

$$q_t = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t, \qquad (4)$$

Table 2. Estimated parameters using Langmuir and Freundlich equations for Cu adsorption at different pHs

pH	Langmuir equation			Freundlich equation		
	Q_{max}, mg kg^{-1}	K, L mg^{-1}	R^2	K_F	b	R^2
5.87	2271.93	0.0121	0.951	135.98	0.446	0.988
3.13	969.89	0.00676	0.967	33.05	0.506	0.950

Table 3. Kinetic parameters for the slow reaction of Cu at different pHs

pH	Lagergren pseudo first-order			Pseudo second-order				Elovich			Intraparticle diffusion		
	q_e	k_1	R^2	q_e	k_2	h	R^2	α	β	R^2	q_e	D/r^2	R^2
						$C_0 = 0.05$ mM							
3.19	28.50	1.147	0.966	31.75	0.0237	23.89	0.9997	5.77×10^3	0.376	0.961	28.60	0.119	0.9768
5.10	31.25	3.798	0.998	31.85	0.210	213.03	1	1.15×10^{38}	2.927	0.6807	38.99	0.159	0.9588
6.92	31.41	4.295	0.9997	31.85	0.224	227.23	1	4.89×10^{74}	5.621	0.9506	39.56	0.159	0.9597
						$C_0 = 0.5$ mM							
3.19	244.68	0.497	0.9254	285.71	0.0013	106.12	0.9978	1.29×10^3	2.78×10^{-2}	0.9799	211.08	8.10×10^{-2}	0.9903
5.10	303.68	2.265	0.9985	312.50	0.0146	1425.78	1	4.13×10^{15}	0.122	0.8711	359.28	0.148	0.9655
6.92	315.04	2.456	0.9998	322.58	0.0240	2497.39	1	3.30×10^{21}	0.162	0.743	378.49	0.150	0.9652

Unit: q_e (mg kg^{-1}), k_1 (d^{-1}), k_2 (kg mg^{-1} d^{-1}), h (mg kg^{-1} d^{-1}), α (mg kg^{-1} d^{-1}), β (kg mg^{-1}), D/r^2 (d^{-1}).

where α is the initial adsorption rate (mg kg^{-1} d^{-1}) and β is the desorption constant (kg mg^{-1}).

Intraparticle diffusion equation can be written as follows:

$$\frac{q_t}{tq_e} = \frac{4\sqrt{\dfrac{D}{\pi r^2}}}{\sqrt{t}} - \frac{D}{r^2}, \qquad (5)$$

where D is the diffusion coefficient (cm d^{-1}), r is the radius of the spherical particle (cm), and the term D/r^2 expresses the apparent diffusion coefficient (d^{-1}).

The pseudo-second order kinetic model was best for the description of the slow reaction of Cu onto Cambisols ($R^2 > 0.997$), and the reaction rate coefficients all increased markedly with increase in soil pH or decrease in initial Cu concentration (Table 3). For example, the values of k_2 at pH 3.19 were 0.0237 and 0.0013 kg mg^{-1} d^{-1}, respectively, for $C_0 = 0.05$ and 0.5 mM; while the values of h were 23.89 and 106.12 mg kg^{-1} d^{-1}, respectively, which was much lower (about 10 and 20 times) than those at pH 6.92. Obviously, during soil acidification the longer time was required for the sorption of more Cu ions; the higher was C_0 (or the lower was pH), the longer time was required to reach an equilibrium. Therefore, when more dissolved Cu (e.g., Bordeaux mixture) was added to a strong acidified soil, higher healthy and environmental risk would occur under strong precipitation or flooding irrigation due to insufficient sorption.

Pseudo-second order equation has been widely applied to describing kinetics of adsorption of metal ions on soils [12, 22, 43, 44, 47], implying that the rate-limiting step may be chemical sorption involving force through sharing or exchange of electrons between Cu ions and the hydroxyl groups of soil surface [47, 56].

Aging moved metals from soil surfaces to deeper in the solid phase through micropore diffusion, surface nucleation/precipitation and occlusion by mineral/SOM, where micropore diffusion was assumed as the rate-limiting step for overall sorption [34, 53, 60]. If initial rapid adsorption (within 24 h) was considered to be from surface nucleation/precipitation, the contribution of micropore diffusion to overall sorption could be assessed by the difference between total sorption amount and adsorption amount within 24 h (Table 4). It could be observed that at strong acidic (pH 3.19) condition, about 40−60% of sorption of Cu was governed by the relatively slow micropore diffusion process; while this contribution ratio was minimal at higher pH (6.92), being less than 10%. These results supported again that Cu sorption on Cambisols with pH was mainly controlled by two mechanisms: surface adsorption and micropore diffusion at low pH; surface nucleation and precipitation at high pH.

pH-dependent Cu transport. Transport of Cu in soil columns were illustrated by breakthrough curves (BTCs) in Fig. 3. Significant retardation or delayed movement of Cu was observed in soil column A with pH 5.87. The BTC was also characterized by low peak concentration ($C/C_0 = 0.64$). The result demonstrated strong retention of Cu in Cambisols under weak acidic condition. In contrast, the BTC of soil column B with pH 3.17 showed little Cu retardation and full breakthrough with peak concentration $C/C_0 = 1$ was observed. In addition, changing pH of introduced Ca(NO$_3$)$_2$ solution from pH 5.87 to pH 3.17 resulted in the release of large amount of residual Cu in column A. These results clearly evidenced that Cu transport in soils was enhanced deep under strong acidic environment.

Mirlean et al. [39] found that soil acidity favored deeper penetration of Cu along the soil profile, and in Arenosol vineyard soils (about pH 4) pesticide-derived Cu reached the groundwater horizon at the depth of about 1.0 m. Strong retention of Cu by soil components such as Fe-, Al-, and Mn-oxides, organic matter and clay minerals made it less mobile [7, 8, 11,
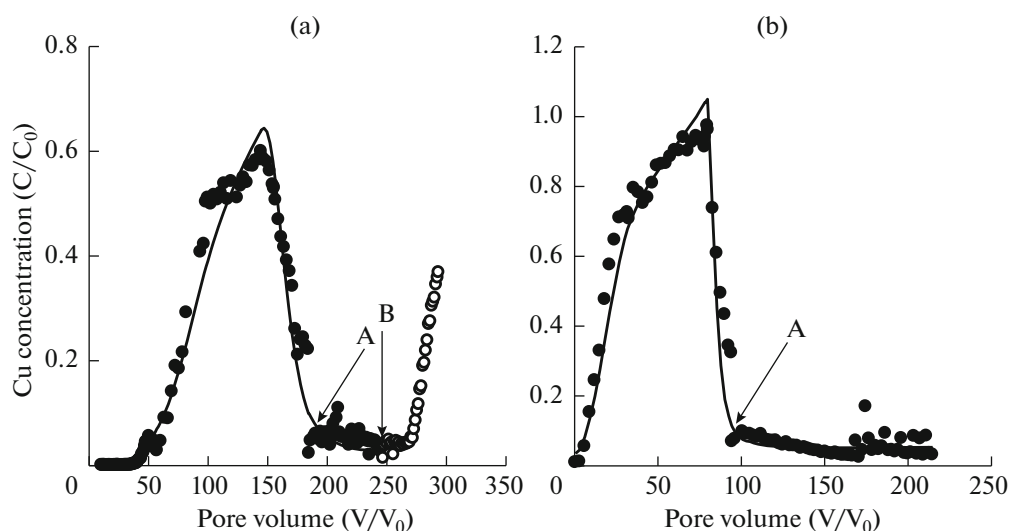
Fig. 3. Breakthrough curves of Cu from Cambisols at (a) pH 5.87 and (b) pH 3.17. The arrow A indicated that the flow interruption occurred when the time lasted for 44 days; and arrow B is that the pH of introduced $Ca(NO_3)_2$ solution was adjusted from pH 5.87 to pH 3.17.

27, 35, 46]; but the retention was highly pH-dependent. Cu adsorption capacity (Q_{max}), affinity (K and K_F), and slow kinetic rate (k_2 and h) all decreased markedly under acidified condition, as shown above, resulted in higher mobility.

In addition, Fig. 3 showed that little Cu was leached by $Ca(NO_3)_2$ solution after 44 days of incubation, suggesting that aging (slowly irreversible reaction) strongly affected Cu transport in soils by reducing the amount of available Cu [45]. So, the irreversible kinetic process must be considered for modeling the reaction and transport of Cu in soils, especially under strong acidic condition as pH < 4. Elbana and Selim [15] have demonstrated that improved predictions could be obtained when nonlinear kinetic irreversible reaction was incorporated into the multi-reaction and transport model (MRTM). However, pH was not considered in the current version of MRTM, which made it unsuitable for simulating the reaction and transport of metals under changing environmental conditions. Geochemical models such as PHREEQC have the ability to simulate the pH-dependent equilibrium sorption but lack the capability of describing the time-dependent sorption and transport processes [25, 37, 41]. Future models should be extended to account for these pH-dependent reaction-transport processes of Cu in acidified soils.

According to the experimental results and other earlier reports [4, 7, 27, 30, 35, 38, 46, 52, 53, 59, 60], a possible mechanism for pH-dependent sorption-transport of added to Cu on acidified soils was proposed as follows (Fig. 4): at higher pH, $CuOH^+$ was sorbed to clay mineral basal surface and edge hydroxyl sites, forming surface precipitates or coprecipitates, which resulted in less mobility of Cu; additionally, weaker complexation between $CuOH^+$ and phenolic hydroxyl of DOM could further weaken the transport of Cu. On the contrary, at lower pH, Cu^{2+} mainly adsorbed to SOM surface and thus diffusion in SOM particles, with higher mobility (especially shorter time

Table 4. The contribution of micropore diffusion to the overall sorption

| Incubation time, d	[Cu]$_0$ = 31.77 mg kg^{-1}						[Cu]$_0$ = 317.73 mg kg^{-1}					
	pH 3.19		pH 5.10		pH 6.92		pH 3.19		pH 5.10		pH 6.92	
	amount, mg kg^{-1}	%	amount, mg kg^{-1}	%	amount, mg kg^{-1}	%	amount, mg kg^{-1}	%	amount, mg kg^{-1}	%	amount, mg kg^{-1}	%
5	5.24	21.07	0.36	1.20	0.13	0.42	70.40	36.71	24.49	8.26	24.56	7.86
10	8.09	29.19	0.81	2.57	0.30	0.97	92.39	43.22	28.61	9.51	25.83	8.23
28	10.18	34.14	1.13	3.57	0.48	1.53	137.21	53.06	35.78	11.62	27.99	8.86
90	11.74	37.42	1.23	3.86	0.80	2.50	158.09	56.56	37.20	12.03	29.72	9.35
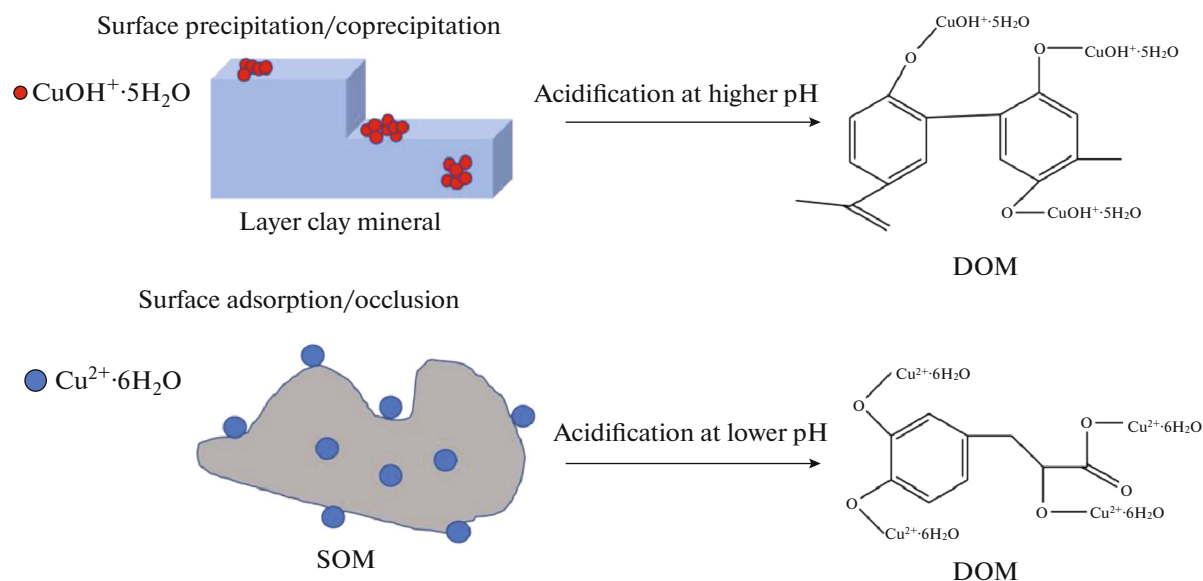
Fig. 4. Possible mechanism for pH-dependent sorption-transport of added Cu.

periods). Which, together with stronger complexation between Cu^{2+} and carboxyl of DOM, would greatly enhance the transport of Cu.

CONCLUSIONS

The pH-dependent sorption and transport of Cu on an acidic brown soil was studied by batch and column experiments. It was shown that Cu adsorption with pH yielded two linear segments with different slopes, where at lower pH Langmuir isotherm fitted better, while at higher pH, Freundlich was better for adsorption. The pseudo-second order kinetic model was better for the description of the slow reaction of Cu onto Cambisols, with lower k_2 and h values (10−20 times lower) and higher contribution of micropore diffusion (40−60% higher) at lower pH than those at higher pH. In addition, the transport of soil Cu showed significant retardation with $C/C_0 = 0.64$ in BTC curves at higher pH; while it was greatly enhanced under acidification (e.g., pH 3.17), with full breakthrough ($C/C_0 = 1$). In summary, two different mechanisms for pH-dependent sorption-transport of added Cu on Cambisols were proposed: at lower pH, Cu^{2+} adsorbed to SOM surface and stronger complexation with DOM, resulting in stronger mobility and transport; while at higher pH, $CuOH^+$ was precipitated on clay mineral surface and weaker complexation with DOM, slowing down the transport of Cu.

CONFLICT OF INTEREST

The authors declare that they have no competing financial interests.

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