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Effects of anions on the capacity and affinity of copper adsorption in two variable charge soils

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Abstract. Effects of nitrate (NO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), and acetate (Ac^-) on Cu^{2+} adsorption and affinity of the adsorbed Cu^{2+} were evaluated in two Fe and Al enriched variable charge soils from Southern China. The maximum adsorption of Cu^{2+} (M, a parameter from the Langmuir isotherm model) in the presence of different anions decreased in the order $Cl^- > Ac^- > NO_3^- > SO_4^{2-}$ for both soils. The clayey loamy soil (mixed siliceous thermic Typic Dystrochrept, TTD), developed on the Arenaceous rock, adsorbed less Cu^{2+} than the clayey soil (kaolinitic thermic Plinthudults, KTP), derived from the Quaternary red earths, regardless of anion type present in the medium. The affinity of adsorbed Cu^{2+} to both soils could be characterized by the Kd (distribution coefficient) values and successive extraction of the adsorbed Cu^{2+} with 1-mol NH_4Ac L^{-1}. The $\log_{10}Kd$ value was smaller for the TTD soil than for the KTP soil and decreased in the order of $Cl^- > NO_3^- > SO_4^{2-} > Ac^-$ at low initial Cu^{2+} concentrations (≤ 40 mg Cu^{2+} L^{-1}), whereas at 80 mg Cu^{2+} L^{-1}, the $\log_{10}Kd$ value was similar for NO_3^-, SO_4^{2-}, and Ac^-, but was slightly higher for Cl^-. Complete extraction of Cu^{2+} adsorbed in the presence of Ac^- was achieved. Influence of NO_3^- and SO_4^{2-} on the affinity of adsorbed Cu^{2+} was similar, but the effects of Cl^- depended on the initial Cu^{2+} concentrations. The extracted percentage of the adsorbed Cu^{2+} in the presence of NO_3^- or SO_4^{2-} increased with increasing Cu^{2+} adsorption saturation. The presence of Cl^-, NO_3^-, or SO_4^{2-} markedly decreased the equilibrium solution pH for both soils with increasing initial Cu^{2+} concentrations, and the delta pH values at the highest Cu^{2+} level were 0.5, 0.63, and 0.55 U for the TTD soil and 0.79, 0.84, and 0.93 U for the KTP soil, respectively for the three anions. The presence of Ac^- had a minimal influence on the equilibrium solution pH because of the buffering nature of the NaAc/HAc medium which buffered the released protons. The effects of anions on Cu^{2+} adsorption and affinity of the adsorbed Cu^{2+} were dependent on anion types and were apparently related to the altered surface properties caused by anion adsorption and/or the formation of anion–Cu^{2+} complexes.

Abbreviations: AAS – atomic absorption spectrometry; Ac^- – acetate; CEC – cation exchange capacity at pH 7.0; Cl^- – chloride; Freundlich equation – $q = k_F C^n$, where q is the amount of adsorbed Cu^{2+}, k_F is a constant related to total adsorption capacity of the soils.; Kd – distribution coefficient; KTP soil – a soil of kaolinitic thermic Plinthudults; Langmuir equation – $q = (k_L M C)/(1+k_L C)$, where q is the amount of adsorbed Cu^{2+}, M is the maximum adsorption of Cu^{2+}, and k_L is a constant related to binding energy; NaAc/HAc medium – a buffering medium consisting of sodium acetate and acetic acid; NH_4Ac – ammonium acetate; NO_3^- – nitrate; rcf – rotational centrifugal force; SO_4^{2-} – sulfate; TTD soil – a soil of mixed siliceous thermic typic Dystrochrept

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Introduction

Adsorption of copper in variable charge soils dominantly occurs on the surfaces of organic matter and Fe, Al, and Mn oxides (Atanassova and Okazaki 1997). This process is highly pH-dependent (Padmanabham 1983; Atanassova 1995; Grossl and Sparks 1995; Atanassova and Okazaki 1997; Al-Sewailem et al. 1999; Christl and Kretzschmar 1999; Khaodhiar et al. 2000; Marosits et al. 2000). Copper adsorption is influenced by pH, surface properties of soil/minerals, contents of organic matter and Fe and Al oxides, CEC, the composition of soil solution, the percentage of base saturation (Msaky and Calvet 1990; Basta and Tabatabai 1992a,b; Atanassova 1995; Echeverría et al. 1998; Christl and Kretzschmar 1999), and other factors such as nature of the media (e.g., liquid/solid ratio, type and concentration of the electrolyte) (Zhu and Alva 1993; Christl and Kretzschmar 1999; Marosits et al. 2000).

Ligand anions can appreciably affect metal adsorption, and to a large extent, the influence is dependent on soil surface properties (Naidu et al. 1997), and the type of anion (Sadusky and Sparks 1991). Cupric nitrate ($Cu(NO_3)_2$) in the electrolyte of nitrate (Grossl and Sparks 1995; Atanassova and Okazaki 1997; Christl and Kretzschmar 1999; Khaodhiar et al. 2000) and $Cu(ClO_4)_2$ in the electrolyte of perchlorate (Basta and Tabatabai 1992a,b; Marosits et al. 2000) were commonly used as copper sources for copper adsorption studies because of the minimal influence of NO_3^- and ClO_4^- on Cu^{2+} adsorption (Padmanabham 1983; Atanassova 1995; Echeverría et al. 1998; Al-Sewailem et al. 1999; Juang and Wu 2002). There are considerable concentrations of natural and synthetic ligand anions in soils, including inorganic (Cl^- and SO_4^{2-}) and organic ligand anions from plant and microbial sources (Naidu et al. 1997) and fertilizers.

The inorganic anions, according to their adsorption characteristics, can be grouped into the following three types: (1) NO_3^-, Cl^-, and ClO_4^- (nonspecific adsorption); and (2) SO_4^{2-} and F^- (specific adsorption with the anions being completely dissociated acids); and (3) PO_4^{3-}, SiO_3^{2-}, and other tetrahedral-forming anions (specific adsorption with anions being incompletely dissociated acids) (Sadusky and Sparks 1991). Generally, NO_3^-, Cl^-, and ClO_4^- are adsorbed as outer-sphere complexes on surfaces with positive charges, but SO_4^{2-} can be adsorbed as both outer-sphere and inner-sphere complexes (Sparks 1995). However, the specific adsorption of Cl^- onto variable charge soils was reported by Wang et al. (1987). Anion adsorption varies with pH, usually increasing with pH and reaching a maximum when the pH is close to the pKa value of the monoprotic conjugate acids (a compound that donates one proton) and slope breaks have been observed at pKa values for anions of polyprotic conjugate acids (a compound that donates more than one proton) (Sparks 1995).

The effects of anions on metal adsorption have been mostly studied in soils from the temperate regions (Naidu et al. 1997). Zhang and Sparks (1996) found no difference in copper adsorption on a Wyoming montmorillonite of a sodium–copper exchange system among the Cl^-, ClO_4^-, NO_3^-, and SO_4^{2-} electrolyte media. Few data have been reported on variable charge soils. Zhang et al. (1998) conducted an experiment with three variable charge soils, two from China and one from Germany and observed that

the addition of SO_4^{2-} invariably increased the adsorption of Zn^{2+} or Cd^{2+} at the pH range of 4–6 when SO_4^{2-} was added prior to the metal ions. In two sandy loam variable charge soils from the middle Atlantic Coastal Plain region, USA, the amount of potassium (K) adsorbed at pH 5 or 6 decreased for different accompanying anions in the order of $SiO_3^{2-} > PO_4^{3-} > SO_4^{2-} > Cl^- > ClO_4^-$ (Sadusky and Sparks 1991). Cadmium adsorption on kaolinite increased in the presence of organic materials, due to formation of an adsorbed organic layer on the clay surface (Haas and Horowitz 1986), which was confirmed by the findings of Alcacio et al. (2001) that Cu^{2+} was bonded to goethite-humate complexes. The adsorption of anions such as SO_4^{2-} and PO_4^{3-} on variable charge surfaces can enhance metal adsorption due to an increase in negative charges (Naidu et al. 1990) and by a similar reaction, organic anions can increase adsorption of Cu^{2+} or Ag^+ on variable charge oxides (Davis and Leckie 1978).

Some data from copper adsorption on pure oxides (abundant in variable charge soils) indicated that copper is bonded in goethite–humate complexes in two ways: at low humate adsorption levels, copper is bonded as a bridging cation between goethite and humate, and at high humate adsorption levels copper is bonded to adsorbed humate directly (Alcacio et al. 2001). The presence of SO_4^{2-} enhanced the adsorption of Cu^{2+} onto goethite, which increased at the equilibrium pH when delta zeta potential decreased to a plateau because of SO_4^{2-} adsorption (Juang and Wu 2002). The stability of Cu^{2+}–acetate is comparable with that of Cu^{2+}–humic acid complexes at relatively high Cu^{2+} adsorption levels (McBride 1989).

However, the effects of anions on adsorption behavior of copper in variable charge soils are not fully understood. It is hypothesized that anions including organic ligands influence adsorption of copper in the variable charge soils and the interactions vary with different anions.

Red soil, a type of variable charge soil widely distributed in southeast China, has an apparent red color with a high content of Fe and Al oxides (usually iron oxides >5%) and low pH ranging from <4.0 to 6.0 (Yu 1997). It is comparable with Oxisols, Ultisols, Alfisols, and Inceptisols according to the USDA soil classification system. The predominant clay mineral of these soils is kaolinite, which only carries about 3–10 cmolc kg^{-1} permanent negative charges as compared with 80–120 cmolc kg^{-1} for montmorillonite, and presents characteristics of variable negative or positive charges. Therefore, soil organic matter and oxides have a great influence on red soil charge characteristics because its clay minerals have a small proportion of negative charges (Yu 1997). Red soils in China have been vastly studied for adsorption of heavy metals, especially copper (Li et al. 2002; Yu et al. 2002). However, the effects of anions on copper adsorption in these soils are not documented. The objective of this study was to investigate the influences of anions including NO_3^-, Cl^-, SO_4^{2-}, and Ac^- (acetate, representing the simple organic anion) on copper adsorption in two variable charge soils that were derived from different parent materials. Adsorption isotherms and change of equilibrium solution pH during copper adsorption were evaluated under laboratory conditions. A Langmuir and a Freundlich model were employed to describe adsorption isotherms of copper, as affected by different anions presented in the electrolyte media. At the same time, the affinity of adsorbed copper was characterized by both the distribution coefficient

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of Cu^{2+} adsorption equilibrium and successive extraction with 1 mol L^{-1} NH_4Ac (pH 5.0).

Materials and methods

Soils. Two variable charge soils were collected at the depth of 0–20 cm from citrus groves in Longyou County, Zhejiang Province, China (E119°02′–120°20′, N28°44′–29°17′). This area enjoys a monsoon climate with annual average temperature near 17 °C and annual rainfall about 1400 mm. The soil of clayey kaolinitic thermic Plinthudults (KTP) was derived from the Quaternary red earths, and the other soil (clayey mixed siliceous thermic typic Dystrochrept, TTD) was developed on the Arenaceous rock (a sedimentary sandstone). The KTP soil has been weathered to a greater degree than the TTD soil according to their clay mineral composition examined using the X-ray diffraction analysis (Yu et al. 2002). Soil samples were air-dried, ground, and sieved to 2 mm and subsamples of air-dried soils were ground and passed through a 0.25 mm sieve for measuring basic properties. Subsamples of each soil were analyzed for: (1) particle-size distribution by a hydrometer method (Liu et al. 1996); (2) mineralogical composition of the clay fraction by X-ray diffraction (Siemens D500 X-ray diffractometer with CuKa at 40 kV and 40 mA); (3) soil pH at a soil/solution ratio of 1:2.5 in both deionized water and 1 mol KCl L^{-1} using a pH meter (Mettler-Toledo MP120, Schwerzenbach, Switzerland); (4) soil organic carbon by a modified Tinsley method (Lu 2000); (5) total exchangeable acidity and exchangeable-Al^{3+} and $-H^{+}$ by the 1 mol KCl L^{-1} extraction–titration method (Liu et al. 1996); (6) cation exchange capacity (CEC) and exchangeable bases by the 1 mol NH_4Cl L^{-1} (pH 7.0) as described by Lu (2000); (7) exchangeable Cu extracted by the 0.1 mol HCl L^{-1} at the soil/solution ratio of 1:5 (Lu 2000) and total Cu by a HF–$HClO_4$ digestion method (Tessier et al. 1979), with the concentrations of Cu in the extracts or digests determined using an atomic absorption spectrometry (AAS) with acetylene/air flame (AA6800, Shimadzu, Kyoto, Japan); (8) contents of free Fe and Al oxides by the citrate–bicarbonate–dithionite method, and amorphous Fe and Al oxides by the ammonium oxalate method (pH 3.2) (Lu 2000), with the concentrations of Fe and Al in the extracts determined by the colorimetric method proposed by Xu and Chen (1980). The effective cation exchange capacity (ECEC) and base saturation were calculated from the exchangeable acidity and bases (K, Na, Ca, and Mg). Selected properties of the soils mentioned-above are given in Table 1.

Sources and concentrations of copper (II).. Four compounds of copper were selected as copper sources for this study: $CuCl_2$, $CuSO_4$, $Cu(NO_3)_2$, and $Cu(Ac)_2$. Eight levels of Cu^{2+} concentrations were applied: 0, 1.0, 2.0, 5.0, 10.0, 20.0, 40.0, and 80.0 mg L^{-1} (equal to 0, 0.02, 0.03, 0.08, 0.16, 0.31, 0.63, and 1.26 mmol L^{-1}). All reagents are analytical grade from chemical companies in China.

Adsorption and proton release. Portions of 2.00 g air-dried soil sample (<0.25 mm) were each weighed into a 100-mL polypropylene centrifuge tube. Fifty

Table 1. Selected physiochemical properties of the variable charge soils (TTD and KTP).

Soil properties	Soils	
	TTD	KTP
Particle size (g kg^{-1})		
Clay (<0.002 mm)	421.0	483.4
Silt (>0.002 and <0.05 mm)	350.1	261.9
Sand (>0.05 mm)	228.8	254.7
Textural class (American textural grade)	Clayey loam	Clay
Main clay minerals*	K, O, C, F	K, O
pH (H$_2$O)/(1 mol KCl L^{-1})	4.86/3.96	5.39/4.33
Total organic carbon (g C kg^{-1})	6.65	9.03
Exchangeable acidity (mmolc kg^{-1})		
Total	41.09	15.20
H$^+$	4.15	0.95
Al^{3+}	36.93	14.25
Exchangeable bases (mmolc kg^{-1})		
Total	77.31	120.0
Ca^{2+}	67.88	102.0
Mg^{2+}	6.79	15.44
K$^+$	2.64	2.64
Na$^+$	nd**	nd
ECEC (mmolc kg^{-1})	118.40	135.20
Base saturation (%)	65.29	88.76
CEC $_{pH\ 7.0}$ (mmolc kg^{-1})	121.22	159.94
Background levels of Cu (mg kg^{-1})		
Total Cu	28.56	85.51
Exchangeable Cu (0.1 mol L^{-1} HCl, 1:5)	1.83	32.34
Oxides of Fe and Al (g kg^{-1})		
Free Fe oxide (Fe)	42.22	36.68
Free Al oxide (Al)	13.04	18.82
Amorphous Fe oxide (Fe)	0.69	1.03
Amorphous Al oxide (Al)	0.98	0.81

*K, kaolinite; O, Fe and Al oxides; C, chlorite; F, feldspar.
** nd means 'not detected'.

milliliters of solution containing 0, 1.0, 2.0, 5.0, 10.0, 20.0, 40.0 or 80.0 mg Cu^{2+} L^{-1} with respect to CuCl$_2$, Cu(NO$_3$)$_2$, Cu(Ac)$_2$, and CuSO$_4$ at an ionic strength of 0.01 mol L^{-1} prepared from NaCl, NaNO$_3$, NaAc, or Na$_2$SO$_4$, were respectively added to each of the centrifuge tubes containing the soil samples. Before they were added to soil samples, pHs of above solutions were adjusted to 5.0 with diluted solution of respective acids, that is, HCl, H$_2$SO$_4$, HNO$_3$ or HAc. The resultant suspensions were shaken at 200 rev min^{-1} for 2 h at 25 °C and equilibrated in a dark incubator at 25 °C for additional 22 h. At the end of designated time, the suspensions were centrifuged at 2500 × g rotational centrifugal force (rcf) for 10 min and filtered through a filter paper (quick mode). Ten milliliters of the filtrates were transferred into a 10-mL polypropylene centrifuge tube for measuring Cu^{2+} concentration (*C*) using the AAS. A standard set of each anion treatment was made

to overcome anion effects on the Cu analysis. Total amounts of adsorbed Cu^{2+} (q) were calculated by the difference between the total applied Cu^{2+} and the soluble Cu^{2+} in the supernatant solutions. The remaining filtrates were used for measuring pH.

Affinity of adsorbed copper. The Cu^{2+}-enriched soil residues separated from the supernatant solutions by centrifugation from the above adsorption experiment were rinsed several times with 95% ethanol (stirred by a vortex and shaken at 200 rpm for 15 min and centrifuged for 10 min at $2500 \times$ g rcf) to remove Cu^{2+} in the entrapped solution until no Cu^{2+} was detected in the leachate (approximately 5 times). The mass balance was performed for each tube and the weight loss was recorded. Fifty milliliters of 1 mol NH_4Ac L^{-1} (pH 5.0) were added to each tube containing the Cu-enriched soil residue. The resultant suspensions were agitated with a vortex, shaken at 200 rpm for 2 h at 25 °C, and then equilibrated for additional 10 h in a dark incubator at 25 °C. At the end of designated time, the suspensions were centrifuged at $2500 \times$ g rcf for 10 min and then filtered. Ten milliliters of the filtrates were pipetted into a 10-mL polypropylene centrifuge tube for measuring Cu^{2+} concentration. The extraction process was repeated five times and the total amount of extracted Cu^{2+} was calculated as the sum of five successive extraction processes. The nonextractable fraction of adsorbed Cu^{2+} in the soils (named as residue) was obtained by the difference between the total adsorbed Cu^{2+} and the total recovered Cu^{2+} by the five successive extractions with the NH_4Ac solution (pH 5.00 ± 0.02).

Statistical analysis. All the data were processed by Microsoft® Excel 2002, and the linear and nonlinear regressions and ANOVA (t-test) were conducted using the program of SAS® (SAS, Institute 1999–2001).

Results and discussion

Copper adsorption isotherms

The presence of different ligand anions in the 0.01 mol L^{-1} sodic electrolyte affected both the capacity and affinity of copper adsorption in the two variable charge soils (Figure 1 and Table 2). In the designed range of initial copper concentrations, all isotherms were close to the type L subtype 2 curve, implying the completion of theoretical monolayer adsorption, whereas the isotherms of both soils in the presence of Cl^- were close to the type L subtype 1 curve, indicating that both soils were not saturated with respect to monolayer adsorption, according to the classification of adsorption isotherms by Giles et al. (1960). The influence of anions on Cu^{2+} adsorption was related to the initial Cu^{2+} concentrations (Table 2). At the low initial Cu^{2+} concentrations (<5 mg L^{-1}), Cu^{2+} adsorption was nearly complete and there was no significant difference between NO_3^- and Cl^- for both soils. On the contrary, the presence of SO_4^{2-} or Ac^- reduced Cu^{2+} adsorption, with Ac^- being more effective in the KTP soil. At the high initial Cu^{2+} concentrations (>5 mg L^{-1}), the percentage of adsorbed Cu^{2+} over the total added Cu^{2+} decreased markedly with increasing initial
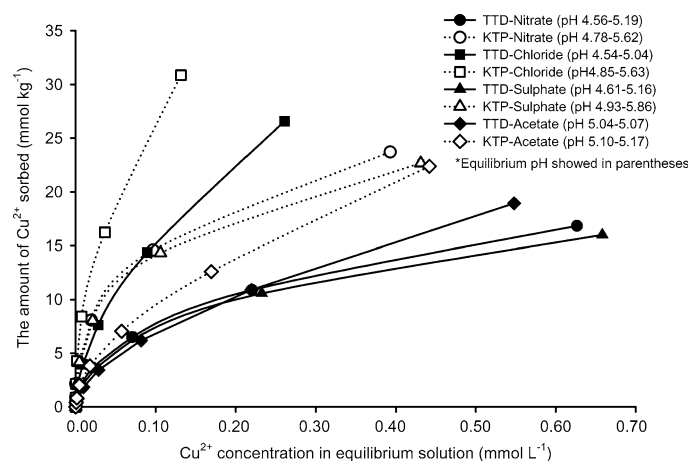
Figure 1. Effect of anions on isotherms of Cu^{2+} adsorption in the two variable charge soils (TTD and KTP).

Table 2. Percentages of adsorbed Cu^{2+} in the total added as a function of Cu^{2+} loading in two variable charge soils (TTD and KTP).

Soils	Initial Cu^{2+} concentration (mg L^{-1})	% of Cu^{2+} adsorbed in the total applied Cu^{2+}			
		Nitrate	Chloride	Sulfate	Acetate
TTD	1	100.0	100.0	100.0	94.8
	2	99.7	100.0	96.2	91.6
	5	93.3	97.5	91.3	87.6
	10	87.1	94.4	84.8	81.9
	20	77.6	91.1	76.3	74.0
	40	65.0	85.8	63.1	65.1
	80	50.3	79.3	47.8	56.5
KTP	1	100.0	100.0	98.3	95.7
	2	100.0	100.0	98.4	95.7
	5	100.0	99.6	98.1	94.1
	10	98.0	99.0	97.1	88.8
	20	93.8	97.7	93.3	81.7
	40	84.7	94.2	83.2	73.1
	80	68.8	89.6	65.8	64.9

Cu^{2+} concentrations in the electrolyte media containing NO_3^-, SO_4^{2-}, or Ac^-, around 50% for the TTD soil and around 66% for the KTP soil at the highest Cu^{2+} added level (Table 2). However, in the electrolyte medium containing Cl^-, the corresponding percentages were 79% and 90%, respectively for the TTD and the KTP soils (Table 2). The Freundlich model ($q = k_F C^n$) consistently provided better fits for all anion treatments than the Langmuir model ($q = (k_L M C)/(1+k_L C)$). The maximum adsorption of Cu^{2+} (M), obtained from the Langmuir model, decreased among the different anions in the order of $Cl^- > Ac^- > NO_3^- > SO_4^{2-}$ for both soils (Table 3).

Results of ANOVA analysis showed that the presence of Cl^- significantly increased copper adsorption ($p < 0.01$), as compared with NO_3^-, SO_4^{2-}, or Ac^-, among which no statistical difference was observed (Table 4). The KTP soil adsorbed more Cu^{2+} than the TTD soil ($p < 0.05$, Table 4), probably because the former had higher pH, CEC (or ECEC), and base saturation, and greater contents of clay and organic matter than the latter (Table 1) (Yu et al. 2002).

Copper speciation in equilibrium solutions was influenced by accompanying anions. The distribution of dissolved and adsorbed Cu species calculated using the Visual MINTEQ (Version 2.2, Gustafsson 2003) varied among the different anions. The added Cu^{2+} was mostly dissolved in the equilibrium solutions in the presence of NO_3^- or Cl^- (up to 98% of total added Cu^{2+} for both TTD and KTP soils), whereas in the presence of SO_4^{2-} or Ac^-, 40% or 48% of the added Cu^{2+}, was presented as complexes with the respective accompanying anion, such as $CuSO_4(aq)$, $CuAc^+$, $Cu(Ac)_2(aq)$, $Cu(Ac)_3^-$ (Table 5). This result was consistent with Cu adsorption in the two variable charge soils. In the sodic electrolytes, the amounts of adsorbed Cu^{2+} in both soils were greater in the presence of Cl^- or NO_3^- than in the presence of SO_4^{2-} or Ac^-, because of greater Cu^{2+} activity in the former medium than in the latter one, in which some Cu^{2+} complexes were formed.

The k_F (L kg^{-1}) from the Freundlich model is related to total adsorption capacity of the soils and the k_L (L mmol^{-1}) from the Langmuir model is a constant related to binding energies (Echeverría et al. 1998). Although the physical meaning of the two parameters are not well defined (Sparks 1995), they may be useful for evaluating adsorption characteristics in different soils. For both tested soils, the k_F values in the presence of Cl^- were two times greater than those in the presence of any other anion. The k_F values changed in the same trend as the M value (the maximum adsorption) (Table 3). Based on the k_L values, the presence of Cl^- resulted in the highest and the presence of Ac^- provided the lowest binding energy of Cu^{2+} adsorption among the tested anions. The presence of NO_3^- or SO_4^{2-} had an intermediate value between Cl^- and Ac^-. The effects of anions on Cu^{2+} adsorption were likely related to the change of soil surface characteristics caused by anion adsorption, as indicated by Zhang et al. (1998) and Alcacio et al. (2001). Li and Ji (2000) reported that the zeta potential of Latosol particles after anion adsorption decreased in the order of $HPO_4^{2-} > F > SO_4^{2-} > Cl^- > NO_3^-$ at pH 3.5–8.0. The zeta potential of goethite was reduced and subsequently, Cu^{2+} adsorption was enhanced by SO_4^{2-} adsorption, whereas a minimal effect on the zeta potential of goethite was observed during the adsorption of Cu^{2+} added as $Cu(NO_3)_2$ (Juang and Wu 2002). These findings confirmed previous reports that NO_3^- has a minimal influence on heavy metal adsorptions on soils or soil minerals. However, in our experiment, the presence of SO_4^{2-} decreased Cu^{2+} adsorption in the two variable charge soils, as compared with NO_3^-, especially at relatively higher initial Cu^{2+} levels. The mechanisms of these phenomena remain unclear.

In addition, anions could form a certain complex with Cu^{2+} before Cu^{2+} is adsorbed. For instance, the formation of monovalent complex, $CuCl^+$ or $CuNO_3^-$ can enhance or reduce copper adsorption onto soils (Zhang and Sparks 1996). In this study, the amounts of Cu^{2+} adsorbed by the two variable-charge soils were higher in the presence of Cl^- than that with any other anion. This might be caused by the formation of monovalent

Table 3. Parameters of copper adsorption in the two variable charge soils (TTD and KTP) at 25 °C.

Soils	Anions	Langmuir equation			Freundlich equation		
		k_L (L mmol^{-1})	M (mmol kg^{-1})	r^2	k_F (L kg^{-1})	n	r^2
TTD	Nitrate	6.66	20.2	0.974	20.7	0.44	0.998
	Chloride	7.18	40.1	0.984	56.0	0.56	0.999
	Sulfate	6.82	18.9	0.981	19.5	0.44	0.998
	Acetate	3.04	29.7	0.987	26.9	0.59	0.999
KTP	Nitrate	18.4	25.9	0.955	33.1	0.36	0.999
	Chloride	27.5	38.0	0.952	74.0	0.44	0.995
	Sulfate	21.2	23.8	0.968	31.8	0.38	0.992
	Acetate	4.07	34.1	0.982	35.3	0.56	0.999

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Table 4. ANOVA (*t*-test) analysis of measured parameters between the two soils (TTD and KTP) and among the four anions.

Items		Equilibrium Cu concentration		Cu adsorption		Residual Cu^{2+}		Log Kd		Delta pH	
		$p < 0.05$	$p < 0.01$	$p < 0.05$	$p < 0.01$	$p < 0.05$	$p < 0.01$	$p < 0.05$	$p < 0.01$	$p < 0.05$	$p < 0.01$
Soil	KTP	b*	ns**	a	ns	b	ns	ns	ns	ns	ns
	TTD	a	ns	b	ns	a	ns	ns	ns	ns	ns
Anion	Nitrate	a	A	b	B	ab	AB	b	B	c	B
	Chloride	b	B	a	A	bc	AB	a	A	b	B
	Sulfate	a	A	b	B	a	A	b	B	bc	B
	Acetate	a	A	b	B	c	B	b	B	a	A

*The different small letters indicate <5% significance level and the capital letter, <1% significance level.
**ns means 'not significant'.

Table 5. Percentage distribution of dissolved and adsorbed Cu species in equilibrium solution as calculated using the Visual MINTEQ.

Cu species*	Soil					
	TTD			KTP		
	Cu^{2+}	Cu–anion complex	$CuOH^+$	Cu^{2+}	Cu–anion complex	$CuOH^+$
Nitrate	97.66(0.08)bA**	2.14(0.13)cC	0.19(0.10)a	97.26(0.21)bB	2.13(0.13)dD	0.58(0.33)aA
Chloride	98.46(0.04)aA	1.36(0.08)dC	0.17(0.07)ab	98.08(0.20)aA	1.35(0.08)cC	0.53(0.28)aAB
Sulfate	59.91(0.11)cB	39.97(0.15)bB	0.12(0.06)b	59.68(0.07)cC	39.84(0.24)bB	0.47(0.27)aAB
Acetate	53.69(1.19)dC	46.16(1.19)aA	0.15(0.01)ab	52.25(0.96)dD	47.57(0.97)aA	0.17(0.01)bB

*Cu^{2+} represents the dissolved species and Cu–anion complex means $CuNO_3^+$, $CuCl^+$, $CuSO_4(aq)$, and total of $Cu(AC)^+$, $Cu(AC)_2(aq)$, and $Cu(AC)_3^-$.
**Data present as 'Mean(SD)', and the small case letter following 'Mean(SD)' means the significant level among anions at $p < 0.05$, and the upper case letter means at $p < 0.01$.

Table 6. The percentages of residual adsorbed Cu^{2+} in two variable charge soils (TTD and KTP) after five successive extraction with 1-mol NH_4Ac L^{-1} (pH 5.0).

Soils	Initial Cu^{2+} concentration (mg L^{-1})	Nitrate (%)	Chloride (%)	Sulfate (%)	Acetate (%)
TTD	1	40.73	79.74	37.79	11.55
	2	29.01	46.61	28.02	3.96
	5	14.54	19.40	22.62	1.14
	10	12.56	9.48	15.07	0.00
	20	11.61	15.83	13.20	0.00
	40	8.12	24.67	8.37	0.00
	80	9.17	41.00	5.80	0.00
KTP	1	14.58	15.39	21.87	4.64
	2	13.42	3.35	17.42	0.00
	5	10.95	0.00	15.92	0.00
	10	10.86	0.00	12.76	0.00
	20	8.82	0.00	11.94	0.00
	40	7.59	3.29	10.41	0.00
	80	7.52	21.58	6.77	0.00

complexes of Cl^- with Ca^{2+} or Mg^{2+} as well as Cu^{2+}, thus, providing more adsorbing sites for Cu^{2+} and enhancing Cu^{2+} adsorption in the soils when higher Cl^- and Cu^{2+} levels were present in the media, as indicated by Sposito et al. (1981) and Hundal and Pasricha (1998) on potassium (K) adsorption. The adsorption of Cl^-, especially specific adsorption of Cl^- onto variable charge soils (Wang et al. 1987), adding negative charges to variable charge surfaces, might be another possibility of the Cl^- effect on the Cu^{2+} adsorption–desorption (Doula and Ioannou 2003). Chloride adsorption occurred during the Cu adsorption by clinoptilolite in the 0.01 mol KNO_3 L^{-1} electrolyte, in which the Cu source was $CuCl_2$, but Cl^- adsorption was lower in the 0.01 mol KCl L^{-1} electrolyte than in the 0.01 mol KNO_3 L^{-1} electrolyte (Doula and Ioannou 2003). This was evidenced by the higher residual Cu^{2+} in the soils treated with higher initial Cu^{2+} concentrations (>10 mg L^{-1} for TTD soil and >20 mg L^{-1} for KTP soil) in the presence of Cl^- after successive extractions with 1 mol NH_4OAc L^{-1} (pH 5.0) (Table 6). The decrease in Cu^{2+} adsorption in the presence of SO_4^{2-} or Ac^- at the low Cu^{2+} concentrations was probably due to a competition between anions and oxide surfaces (or other variable charge surfaces) for Cu^{2+} (McNaughton and James 1974).

The capacity of variable charge soils to adsorb/desorb Cu^{2+} is fundamental to Cu transport and bioavailability, even biotoxicity. The variable charge soils usually have a smaller amount of surface negative charges than the permanent charge soils (Li et al. 2002). Therefore, the capacity of Cu^{2+} adsorption is credibly smaller in the variable charge soils than in the permanent charge soils at a same size of the specific surface area. Anion adsorption on the variable charge surface, especially specific adsorption, such as Cl^- (Wang et al. 1987; Doula &d Ioannou 2003), could increase negative charges onto the surface, subsequently, enhancing Cu^{2+} adsorption or reducing Cu^{2+} desorption.
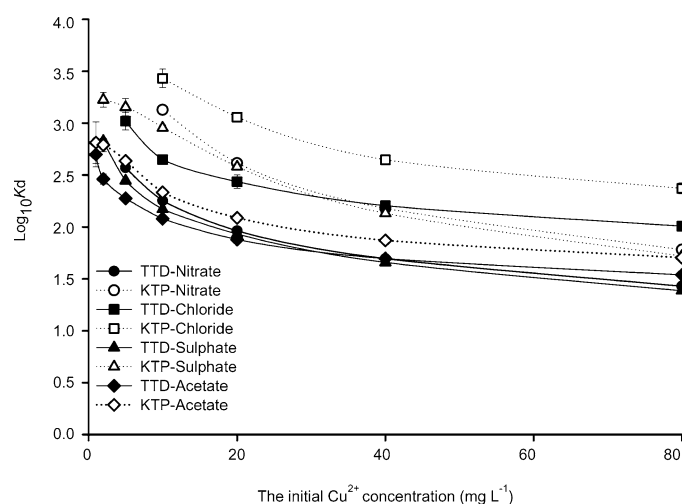
Figure 2. Effect of anions on the distribution coefficient (Kd) of Cu^{2+} adsorption in the two variable charge soils (TTD and KTP). Error bars mean standard deviation (SD).

Distribution coefficient (Kd) of Cu^{2+} and affinity of adsorbed Cu^{2+} to soils

The distribution coefficient (Kd) of Cu^{2+} between soil and the solution reflects the overall affinity between Cu^{2+} and the surfaces of soil constituents (Atanassova 1995; Wang 1995). The KTP soil had a slightly higher $log_{10}Kd$ than the TTD soil for all the electrolyte media used (Figure 2). The KTP soil had a greater content of organic matter and clay, and higher pH and CEC (Table 1) and thus, adsorbed more Cu^{2+} than the TTD soil, but no statistical difference in $Log_{10}Kd$ was observed between the two soils (Table 4). The Kd values at the low levels of added Cu^{2+} were not obtained because the added Cu^{2+} was almost completely adsorbed or the Cu^{2+} concentrations in equilibrium solution were below the detection limit of the AAS (Table 2). The $Log_{10}Kd$ values exponentially declined with increasing initial Cu^{2+} concentrations (Figure 2). This can be attributed to a high affinity of Cu^{2+} to those highly selective sites (specific adsorption) at the low initial Cu^{2+} concentrations, followed by adsorption of Cu onto those less selective sites (nonspecific adsorption) (Basta and Tabatabai 1992a). Copper precipitation (or co-precipitation) on soil surfaces (Karthikeyan et al. 1999) might happen at the high initial Cu^{2+} additions when all adsorbing sites were completely occupied. Lehmann and Harter (1984) reported that Cu^{2+} was mainly adsorbed onto the low binding-energy sites at the Cu^{2+} levels exceeding 100 mg Cu kg^{-1} soil in a comparable soil. These sites could adsorb Cu^{2+} through electrostatic forces or by forming type A or type B ternary surface complexes (Alcacio et al. 2001).

The influence of anions on the Kd values was dependent on the initial Cu^{2+} concentrations (Figure 2). The $Log_{10}Kd$ values decreased in the order of $Cl^- > NO_3^- > SO_4^{2-} > AC^-$ at the initial Cu^{2+} concentrations ≤ 40 mg Cu^{2+} L^{-1}.

At the initial Cu^{2+} concentration of 80 mg Cu^{2+} L^{-1}, the $Log_{10}Kd$ value was hardly affected by the tested anions except for Cl^-, which resulted in a relatively greater $Log_{10}Kd$ values ($p < 0.01$, Table 4). The differential effect between Cl^- and other anions on Cu^{2+} adsorption might be due to the formation of complexes of Cl^- with Ca^{2+} or Mg^{2+}, which released additional adsorption sites for Cu^{2+}, or due to the adsorption of Cl^- which increased negative charges on the variable charge surface (Wang et al. 1987).

In order to determine the affinity of adsorbed Cu^{2+} in the two variable charge soils, the 1-mol NH_4Ac L^{-1} (pH 5.0) was employed to successively extract the adsorbed Cu^{2+} from the Cu^{2+}-enriched soils. The advantage of using this reagent is the formation of copper–acetate complex, which prevents re-adsorption of the re-leased Cu^{2+}. However, this reagent might increase system pH for acidic soils and cause precipitation of cupric hydroxide. In order to prevent a Cu^{2+} precipitation reaction during the extraction process, the pH of the extractant was adjusted to 5.0 using glacial acetic acid, which is comparable to the pH of adsorption equilibrium solutions (4.5–5.8). The measured pH of the extraction equilibrium solutions was 5.00 ± 0.05, indicating that system pH was relatively stable during the extraction process. Presented in Table 6 are the percentages of residual Cu^{2+} in soils after five successive extractions. For both soils, the adsorbed Cu^{2+} in the electrolyte medium of Ac^- was almost completely extracted by the 1 mol NH_4OAc L^{-1} (Table 6), indicating that in the presence of Ac^-, Cu^{2+} ions were weakly bound to soil surfaces. The Cu^{2+} might be adsorbed in the form of cupric–acetate ternary complexes on the soil surfaces, similar to the Type A and B ternary complexes (Alcacio et al. 2001). In the presence of NO_3^- or SO_4^{2-}, the extractable Cu^{2+} by the 1 mol NH_4Ac L^{-1} (pH 5.0) increased with increasing initial Cu^{2+} concentrations. However, in the presence of Cl^-, at the low initial Cu^{2+} concentrations (<10 mg Cu^{2+} L^{-1}), the residual percentages of adsorbed Cu^{2+} decreased with increasing initial Cu^{2+} concentrations, whereas at the high initial Cu^{2+} concentrations (>10 mg Cu^{2+} L^{-1}), the reverse was true (Table 6). Both soils had the same trend, though with different values. The TTD soil had higher affinity for Cu^{2+} than the KTP soil, and therefore, retained more residual Cu^{2+} than the KTP soil after five successive extractions with the 1 mol NH_4Ac L^{-1} (pH 5.0) solution at the initial Cu^{2+} concentrations <10 mg Cu^{2+} L^{-1} (Table 6) and the difference was significant ($p < 0.05$, Table 4).

The results from Kd estimation and extraction of adsorbed Cu^{2+} with the 1 mol NH_4Ac L^{-1} (pH 5.0) solution indicated that in the presence of Ac^-, adsorption of Cu^{2+} on soil surface was loosely bound through the formation of ternary complexes or electrostatic attraction and the affinity of adsorbed Cu^{2+} to soils was the lowest among the tested anions. Sulfate had a small influence on Cu^{2+} adsorption affinity if NO_3^- treatment was considered as a control. The effects of Cl^- on the adsorption affinity of Cu^{2+} likely depended on the initial Cu^{2+} concentrations. The TTD soil generally had a higher affinity for Cu^{2+} than the KTP soil.
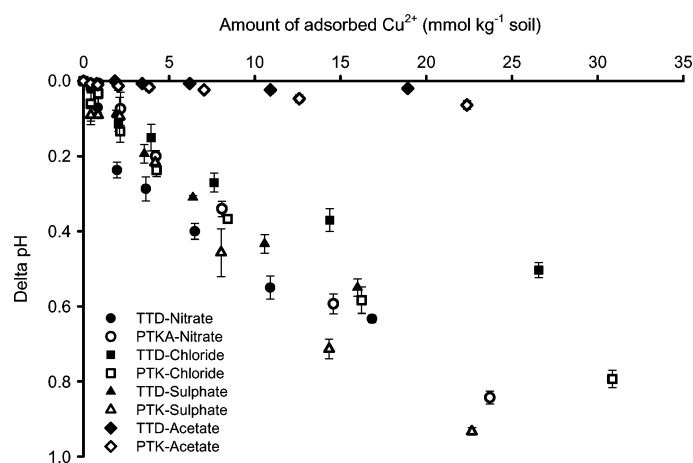
Figure 3. Effect of anions on pH decline of equilibrium solution during Cu^{2+} adsorption in the two variable charge soils (TTD and KTP). Error bars mean standard deviation (SD).

Equilibrium solution pH

It is well known that Cu^{2+} adsorption causes proton release in variable charge soils, and thus reduces the equilibrium solution pH (Marosits et al. 2000). The released proton during Cu^{2+} adsorption can be from the cation exchange, Cu^{2+} hydrolysis, and Al^{3+} hydrolysis when the adsorbed Al^{3+} was replaced by Cu^{2+} (Basta and Tabatabai 1992b; Yu, et al. 2002). The presence of different anions affected the equilibrium solution pH at the range of initial Cu^{2+} concentrations (Figure 3). The decrease in equilibrium solution pH with increasing initial Cu^{2+} concentrations varied among the different anions present in the electrolyte medium for both soils. The type of anions obviously affected the pH value of Cu^{2+} adsorption equilibrium solution (Table 4). At the highest Cu^{2+} level, the equilibrium solution pH decreased by 0.50, 0.63, and 0.55 U for the TTD soil and 0.79, 0.84 and 0.93 U for the KTP soil in the presence of Cl^-, NO_3^-, or SO_4^{2-} (Figure 3). The presence of acetate did not cause a significant decrease in solution pH because the electrolyte medium consists of 0.01 mol L^{-1} NaAc/HAc (pH 5.0), which has a strong buffering capacity.

The pH drop with Cu adsorption in the presence of Cl^-, NO_3^-, or SO_4^{2-} electrolytes might raise some questions regarding the fit of the Freundlich or Langmuir model to Cu^{2+} adsorption in the variable charge soils, for the two isotherm models do not account for pH changes. However, Cu speciation in equilibrium solutions using the Visual MINTEQ (Gustafsson 2003) revealed that the equilibrium pH change in this study, ranging from 4.5 to 5.2 for the TTD soil and from 4.7 to 5.9 for the KTP soil, did not change the distribution of Cu species in equilibrium solutions, whereas the present of different accompanying anions resulted in significant differences in Cu speciation, such as between Cl^-/NO_3^- and SO_4^{2-}/Ac^-, according to

the statistical analysis (Table 5). In order to focus on the effects of accompanying anions on Cu^{2+} adsorption in the variable charge soils, it might be inappropriate to adjust equilibrium solution pHs because pH adjustment of Cu adsorption equilibrium solutions would cause varied anion concentrations among different Cu levels and between the soils since the amount of proton releases varies with the amount of Cu adsorption.

Conclusions

The capacity and affinity of Cu^{2+} adsorption in the two variable charge soils were affected by NO_3^-, Cl^-, SO_4^{2-}, or Ac^- present in the sodic electrolyte solutions. The maximum adsorption (*M*) of Cu^{2+} obtained from the Langmuir model decreased in the order of $Cl^- > Ac > NO_{3-} > SO_4^{2-}$. The affinity of Cu^{2+} to the soils characterized by the distribution coefficient (Kd) and the successive extraction by 1-mol NH_4Ac L^{-1} showed similar results. The $\log_{10}Kd$ value decreased in the order of $Cl^- > NO_3^- > SO_4^{2-} > Ac-$ at the initial Cu^{2+} concentrations $\leq$ 40 mg Cu^{2+} L^{-1}. The percentage of residual adsorbed Cu^{2+} after the successive extraction had no significant difference in the presence of SO_4^{2-}, NO_3^-, or Cl^-, but a complete extraction was achieved in the presence of Ac^-. These results suggest that the effects of anions on adsorption characteristics and affinity of Cu^{2+} adsorption in the variable charge soils are likely related to changes in surface properties caused by anion adsorption, the formation of Cu^{2+}–anion complexes, and the mode of the complexes bound to the surfaces of soil constituents.

Acknowledgements

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