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Mechanism and kinetics of aluminum dissolution during copper sorption by acidity paddy soil in South China

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ABSTRACT

Soil aggregates were prepared from a bulk soil collected from paddy soil in the Taihu Lake region and aluminum (Al) dissolution, solution pH changes during copper (Cu²⁺) sorption were investigated with static sorption and magnetic stirring. Kinetics of Cu²⁺ sorption and Al dissolution were also studied by magnetic stirring method. No Al dissolution was observed until Cu²⁺ sorption was greater than a certain value, which was 632, 450, 601 and 674 mg/kg for sand, clay, silt, and coarse silt fractions, respectively. Aluminum dissolution increased with increasing Cu²⁺ sorption and decreasing solution pH. An amount of dissolved Al showed a significant positive correlation with non-specific sorption of Cu²⁺ ($R^2 > 0.97$), and it was still good under different pH values ($R^2 > 0.95$). Copper sorption significantly decreased solution pH. The magnitude of solution pH decline increased as Cu²⁺ sorption and Al dissolution increased. The sand and clay fraction had a less Al dissolution and pH drop due to the higher ferric oxide, Al oxide and organic matter contents. After sorption reaction for half an hour, the Cu²⁺ sorption progress reached more than 90% while the Al dissolution progress was only 40%, and lagged behind the Cu²⁺ sorption. It indicated that aluminum dissolution is associated with non-specific sorption.

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Introduction

Heavy metal pollution and acidification are two major problems of the soil environment in the Taihu Lake region (Jiang et al., 2012; Wang et al., 2013). Research has showed that soil Al dissolution has an extremely close relation with soil acidification (Dijkstra and Fitzhugh, 2003). Aluminum in the soil mainly exists in the crystal lattice of the aluminum silicate minerals such as feldspar and mica, and other aluminum is in the form of water-soluble state, exchangeable state and organic combined state, and soil environmental changes will lead to aluminum activation and release (Shao et al., 1998). The current Al dissolution studies are focused on

the effects of simulated acid rain and organic acids on soil Al dissolution (Klugh-Stewart and Cumming, 2009; Rosenberg and Butcher, 2010). The findings suggested that Al dissolution increased significantly when the soil pH reduced. Other studies have found that heavy metal ion sorption process by soil would lead to Al dissolution, the release of H⁺, and the decline of soil solution pH. Yu et al. (2002) found significant drops in red soil pH during Cu²⁺ isothermal adsorption. Aoyama et al. (1993) observed that Cu²⁺ additions significantly aggravated soil acidification. Besides, Speir et al. (1999) noticed that adding 10–100 mmol/kg Cu²⁺ and other metal nitrates markedly reduced soil pH in New Zealand soils. Moreover, Xie (1996) showed that soil acidification induced by

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Cu^{2+} additions was due not only to the H^+ exchange, but also to the Al dissolution. The results above all demonstrated that the amount of Al dissolution had a significant positive correlation with the concentrations of added Cu^{2+} . But the mechanism of Al dissolution for heavy metal ion sorption process and H^+ release is not yet clear, and the kinetics has not been discussed in detail.

Soil acidification and Al dissolution both have potentially toxic effects on terrestrial vegetation, and have always been one of important soil environmental chemistry topics. Heavy metal pollution in southern China is often accompanied by soil acidification. Therefore, the objective of the present study is to examine the Al dissolution and the dynamics of soil solution pH during Cu^{2+} sorption by bulk soil and aggregates of paddy soil from the Taihu Lake region. The results would advance our understanding of Al dissolution mechanisms during Cu^{2+} sorption, and also provide theoretical guidance of controlling soil acidification under soil pollution by heavy metals.

1. Materials and methods

1.1. Soil samples

Paddy soil was collected at a depth of 0–20 cm from Jinjiaba Township, Suzhou, Jiangsu Province (31°5'N, 120°46'E), and stored in a 4°C refrigerator. Four particle size fractions (coarse sand: 2.00–0.25 mm, fine sand: 0.25–0.02 mm, silt: 0.02–0.002 mm and clay: <0.002 mm) were separated following the wet sieving and pipette methods (Stemmer et al., 1998; Wang et al., 2009).

1.2. Experiments

1.2.1. Cu^{2+} sorption and Al dissolution

Soil samples (1 g) were weighted into 50 mL centrifuge tubes and 20 mL of Cu^{2+} solutions (0, 10, 20, 40, 80, 120, 160, and 200 mg/L) prepared with a 0.01 mol/L KCl solution was then added. The solution pH was adjusted to 5.50 by 0.01 mol/L HCl or NaOH, which was close to the soil pH (KCl). All tubes were shaken to equilibrate in a constant temperature shaker at $25 \pm 0.2^\circ\text{C}$ for 24 hr. The suspension was then centrifuged at 5000 r/min for 10 min and filtered through a 0.45 μm filter (Huang et al., 2014). The concentrations of Al^{3+} in the supernatants were determined by Optima-2100 Inductive Couple Plasma Atomic Emission Spectrometer (ICP-AES) and the concentrations of Cu^{2+} quantified by Hitachi Z-2000 atomic absorption spectrophotometer (AAS). Adsorbed Cu^{2+} was obtained from the differences between the initial and the final Cu^{2+} concentrations. The supernatant pH was measured by a pH meter (Orion-868, United States) with 0.01 mol/L KCl solution as the blank.

1.2.2. Cu^{2+} desorption

For Cu^{2+} desorption, the precipitates from the above sorption experiment were dispersed in 20 mL of 0.01 mol/L⁻¹ KCl solution and shaken for 24 hr. After shaking, the mixtures were centrifuged at 4000 r/min for 10 min. Subsequently, the concentrations of Cu^{2+} in the supernatants were determined. The Cu^{2+} desorbed by KCl was non-specific sorption (Galunin et al., 2014).

1.2.3. Al^{3+} dissolution at different pH values

Following the same method as above, Al dissolution experiment was conducted at 25°C using 80 mg/L Cu^{2+} at different pH (3.5, 4.0, 4.5, 5.0, 5.5, 6.0, and 6.5 adjusted with 0.01 mol/L HCl or NaOH). The Al^{3+} concentrations in the solution were used to calculate the amount of Al dissolution. The experiment repeated three times. The 0.01 mol/L KCl solution was employed as the blank.

1.2.4. Kinetics of Cu^{2+} sorption and Al dissolution

Bulk soil and different aggregate fractions (2 g) were placed into 250 mL conical flasks, and then 200 mL of 0.01 mol/L KCl solution containing 80 mg/L Cu^{2+} added. The suspensions were shaken at 160 r/min and $25 \pm 0.2^\circ\text{C}$. At 5, 10, 20, 30, and 40 min, and 1, 2, 4 and 8 hr, 1.5 mL suspension was extracted with a syringe, and filtered through a 0.45 μm micro membrane (within 10 s). The concentrations of Cu^{2+} and Al in the solution were measured. The quality control was assured using 0.01 mol/L KCl solution containing standard Cu^{2+} . The experiment was performed in triplicate.

1.3. Analytical methods

Basic properties of soil samples were determined following the conventional laboratory methods described by Lu (2000). Soil pH was measured using a Mettler Toledo pH meter with solution/soil ratio of 2.5:1 (V/V). Soil organic matter (SOM) was determined by wet $\text{K}_2\text{Cr}_2\text{O}_7$ digestion method and free iron oxyhydrates (Fed) by dithionite–citrate–bicarbonate (DCB) extraction. Cation exchange capacity (CEC) was estimated with 0.1 mol/L BaCl_2 . Active Al and exchangeable -H/-Al were quantified with 0.1 mol/L oxalic acid–ammonium oxalate and KCl solution extraction, respectively. The properties of soil samples are shown in Table 1.

1.4. Quality control and statistical analysis

To ensure the accuracy of determination, background adsorption was subtracted with the recommended approaches according to the users' manual. Standard 1000 $\mu\text{g/mL}$ Cu^{2+} solution (GSB G62024-90/2902) and Al^{3+} solution (GSB 04-1713-2004) purchased from the National Standard Material Center was used as the internal standard. All chemical reagents used were of GR grade. All the experiments were carried out in triplicates and the average values were reported. The recoveries of Cu^{2+} and Al^{3+} ranged from 97.5% to 102.3% and the coefficient of variation was less than 10%.

All data were processed using Microsoft Excel 2007. Statistical analyses were conducted using SAS 9.2. The results were plotted by Origin 8.0. Significance of the differences among fractions or treatments was defined at $p < 0.05$.

2. Results and discussion

2.1. Static sorption of Cu^{2+}

2.1.1. Relationship between Al dissolution and Cu^{2+} sorption

In 0–200 mg/L of solution Cu^{2+} concentrations, no Al dissolution was detected in the equilibrium solution until the amount of

Table 1 – Basic properties of soil aggregates.

Size fractions	pH (KCl)	SOM (g/kg)	Ald (g/kg)	Fed (g/kg)	Exchangeable-H (g/kg)	Exchangeable-Al (g/kg)	Active-Al (g/kg)	CEC (cmol(+)/kg)
Sand fraction	5.31 ± 0.03b	36.32 ± 0.18b	4.33 ± 0.13b	29.02 ± 3.08a	46.83 ± 1.21a	1.44 ± 0.12d	1.82 ± 0.16b	21.40 ± 2.22b
Coarse silt fraction	5.75 ± 0.15a	25.72 ± 0.41c	2.06 ± 0.16c	14.34 ± 0.10c	16.23 ± 2.32c	3.33 ± 0.15b	1.31 ± 0.29c	16.69 ± 2.42c
Silt fraction	5.52 ± 0.02c	28.64 ± 0.05b	3.69 ± 0.18b	19.21 ± 0.22b	12.64 ± 5.27c	4.32 ± 0.26a	1.85 ± 0.91b	15.36 ± 3.11c
Clay fraction	5.63 ± 0.06b	46.94 ± 0.08a	5.13 ± 0.14a	32.01 ± 0.41a	26.14 ± 3.24b	2.39 ± 0.25c	2.57 ± 0.15a	47.32 ± 2.14a

Different letters in a same row indicated a significant difference between the fractions of a single soil at $p < 0.05$.

Cu^{2+} sorption was greater than a certain value. This value was 632, 450, 601 and 674 mg/kg for sand, clay, silt, and coarse silt fractions, respectively. The amount of Al dissolution significantly increased as Cu^{2+} sorption increased. The maximum Al dissolution was 572, 919, 840 and 592 mg/kg for sand, clay, silt, and coarse silt fraction, respectively (Fig. 1). Research has showed that Cu^{2+} is first chelated with high affinity sorption sites, *e.g.* organic functional groups such as carboxyl and phenolic hydroxyl, producing strong specific-sorption (Galunin et al., 2014). As Cu^{2+} sorption increased, exchange sorption gradually occurred. In a study on Cu^{2+} contamination in red soil, Yu et al. (2002) found that Al dissolution was not detected until the initial concentration of Cu^{2+} reached 750 $\mu\text{mol/L}$, at which the amount of sorbed Cu^{2+} was about 380 mg/kg. They inferred that the affinity of cations such as K^+ , Ca^{2+} , and Mg^{2+} with soil colloids was less than that of $\text{Al}^{3+}/\text{H}^+$ with soils, and the cations were thus exchanged prior to $\text{Al}^{3+}/\text{H}^+$ when Cu^{2+} sorption was low. Copper ion could replace $\text{Al}^{3+}/\text{H}^+$ only at higher sorption. In Al fractionation, Hargrove and Thomas (1981) found that CuCl_2 could extract not only inorganic, poly and hydrous Al, but also Al bound to organic matter and interlayer of minerals.

Under the same conditions, the maximum Al dissolution was found in the coarse silt fraction, followed by the silt fraction and sand fraction and the least in the clay fraction. Such sequence was opposite to the order of free and amorphous Al oxides in four fractions. Clay and sand fractions had higher CEC and exchangeable bases, but lower exchangeable Al and exchangeable acid (Table 1). Cations such as K^+ , Ca^{2+} , and Mg^{2+} were exchanged by Cu^{2+} prior to $\text{Al}^{3+}/\text{H}^+$. In addition, these

two fractions also contained higher ferric oxide and organic matter, which might inhibit Al dissolution. Ferric oxide has been considered to cover parts of Al-containing minerals in the form of coating, thus reducing the area of these minerals exposed to the solution. Organic matters could also form complex with Al-containing minerals, reducing their active surface area. In addition, organic matters especially macromolecular humus acid containing many active groups, could have complexation reaction with Al, enhancing soil's ability to stabilize Al (Qin and Chen, 1998). Also, Fe and Al oxides content in soil and the differences of crystal shape, could lead to the different release quantity of Al^{3+} in soil (Harrington et al., 2003). Zhu et al. (2002) studied protonation and Al dissolution in red soil and found that iron oxide had a shielding effect on the soil, thus blocking Al release. Therefore, soil ferric oxide and organic matters have protection effects on soil Al dissolution.

2.1.2. Relationship between Al dissolution and Cu^{2+} non-specific sorption

Ion sorption can be divided into specific and non-specific sorption depending on its mechanisms. In the present study, non-specifically sorbed Cu^{2+} was defined as Cu^{2+} desorbed by 0.01 mol/L KCl from soil particles, and the residue was the specifically sorbed Cu^{2+} (Galunin et al., 2014). Regression of Al dissolution with Cu^{2+} sorption (Cu^{2+} specific sorption and non-specific sorption) showed that there was a significant correlation between Al dissolution and Cu^{2+} non-specific sorption ($R^2 > 0.9665$, $P < 0.01$) (Fig. 2). It implied that Al dissolution mainly occurred during the process of non-specific sorption of

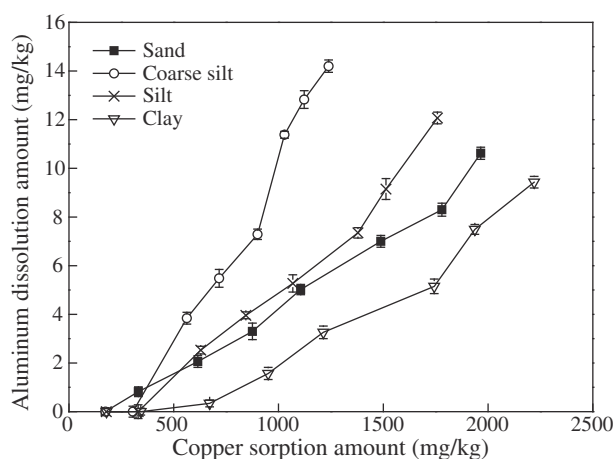


Fig. 1 – Isothermal curves of Al dissolution and Cu^{2+} sorption by soil aggregates at pH = 5.5.

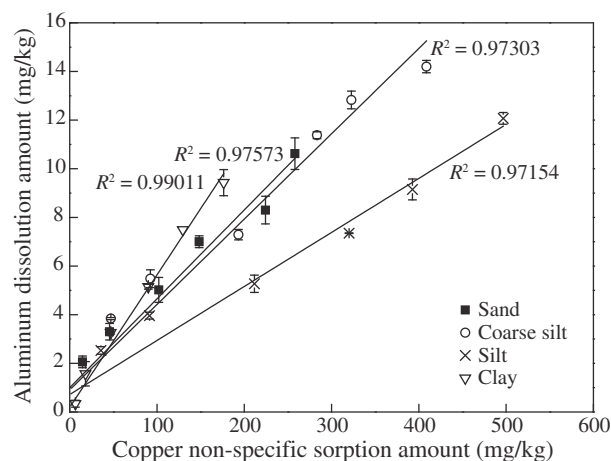


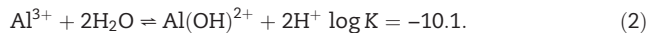
Fig. 2 – Relationship between Cu^{2+} non-specific sorption and aluminum dissolution at pH = 5.5.

Cu^{2+} . The specific sorption of Cu^{2+} occurred first, and the non-specific sorption (exchange sorption) became dominated when the solution Cu^{2+} concentrations exceeded a certain threshold (Basta and Tabatabai, 1992). The exchangeable bases and exchangeable Al ion (H^+) were then replaced by Cu^{2+} . This was in agreement with the above results that no or little Al was detected in the equilibrium solution when small amount of Cu^{2+} was adsorbed by soil aggregates.

2.1.3. Relationship between Al dissolution and equilibrium solution pH

There was a significant positive correlation between Al dissolution and pH decline during Cu^{2+} sorption by soil aggregates. The changes in solution pH (ΔpH) increased quickly with Al dissolution and then gradually flattened. Yu et al. (2002) studied soil solution pH changes at 0–80 mg/L Cu^{2+} during isothermal adsorption and found that the amount of Al dissolution and Cu^{2+} sorption had a significant correlation with ΔpH ($R^2 > 0.97$). In our present experiment, Al dissolution increased curvedly with ΔpH (Fig. 3).

In soil solution, Al ion can exist in the form of Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$ or $\text{Al}(\text{OH})_4^-$, depending on the solution pH (Liu et al., 2007). In the present experimental system, the solution pH ranged from 4.2 to 5.0. The predominant Al forms were Al^{3+} , $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$ (Nordstrom and Howard, 1989). Hydrolysis of Al ion in aqueous solution is as follows:



The more the Al is dissolved, the more the H^+ would be hydrolyzed, thus causing solution pH to decrease more obviously. Declined solution pH would thus promote Al release. Soil solid phase containing Al consumed H^+ by means of Al dissolution, preventing further reduction of the solution pH (Beyrouthy et al., 2000). For example, the solubility of soil organic complexing aluminum under acid condition was affected by the pH and also under the control of the aluminum complexation mechanism (Yamada et al., 2002; Weng et al., 2002). Hence, Al

dissolution and pH decline were a mutually influential process during Cu^{2+} sorption.

At the same amount of Al dissolution, the solution pH drop was the greatest for coarse silt fraction, followed by silt, sand, and clay fractions sequentially. This was directly related to their buffering capacity. Sand and clay fractions contained more organic matter and free iron oxides, and thus had greater buffering of soil solution pH. At low concentrations of Cu^{2+} , no Al was dissolved, but solution pH still declined (Fig. 4). This was because there was more H^+ released during Ca^{2+} sorption (Yu et al., 2002). While studying Ca–H–Al exchange in soil, Guo et al. (2006) found that soil released H^+ mainly via Ca–H exchange mechanism when $\text{Ca}^{2+} < 0.5$ mmol/L. However, when $\text{Ca}^{2+} > 0.5$ mmol/L, the release of H^+ significantly reduced. Due to the Ca–Al exchange, Al^{3+} in the leachate increased obviously with increasing Ca^{2+} concentrations, and the solution H^+ came mainly from Al hydrolysis during this process. This was similar to that of our experiment.

2.1.4. Aluminum dissolution during Cu^{2+} sorption at different pH

In order to further investigate the relationship between Al dissolution and Cu^{2+} sorption as well as the influence of pH on Al dissolution, Cu^{2+} specific and non-specific sorption were determined in 80 mg/L Cu^{2+} solution at different pH, with 0.01 mol/L KCl solution of the same pH as reference. The results showed that Al dissolution caused by Cu^{2+} increased significantly as the pH reduced. At pH = 3.5, Al dissolution in sand, clay, coarse silt and silt fractions was 15.2, 12.3, 24.5, and 31.6 mg/kg, respectively. However, Al dissolution by KCl was far less at the same pH. When solution pH increased to 5.5, KCl-induced Al dissolution was extremely low, with no Al detected in sand and clay fractions, indicating that K^+ almost had no effect on soil Al dissolution. Aluminum in soils is present in the form of aluminosilicate and Al hydroxide. It is difficult for salts such as KCl to replace Al. However, Al may be converted to Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$ or $\text{Al}(\text{OH})_4^-$ when soil pH declines (He et al., 1998). Many studies on the impact of acid rain or organic acids on Al dissolution have showed that Al dissolution suddenly increases when pH drops to 3.0 (Li et al.,

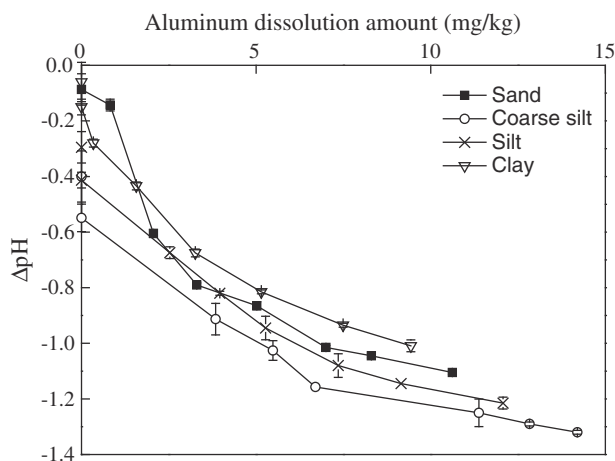


Fig. 3 – Relationship between Al dissolution and pH change at Cu^{2+} of 80 mg/L.

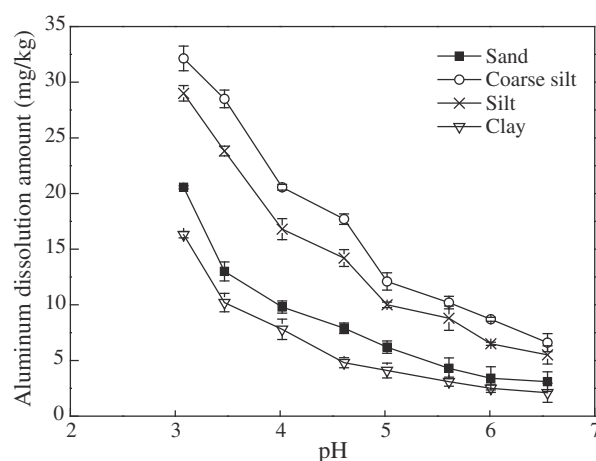


Fig. 4 – Relationship between Al dissolution and solution pH at Cu^{2+} of 80 mg/L.

2006). Under strong acidic soil environment, protons and soil cations had an ion exchange reaction to convert exchangeable hydrogen into exchangeable aluminum. proton ions reacted with different forms of Al, activating Al ions and thus increasing soil exchangeable Al. Copper added to such soils would release Al ions to the soil solution (Zhu et al., 2002).

While investigating the relationship between Al dissolution and total sorption, specific sorption, and non-specific sorption of Cu^{2+} at 40 mg/L under different pH, we found that the Al dissolution had a poor correlation with Cu^{2+} total sorption and specific sorption, but significant correlation with Cu^{2+} non-specific sorption (Fig. 5, $R^2 > 0.90$, $p < 0.05$). Generally, with the increase of soil solution pH, negative charge on soil surface increased but positive charge reduced, and the increase of hydration degree of Cu^{2+} made the Cu^{2+} sorption rate increased with increase with pH (Fernández-Calviño et al., 2008; Pérez-Novio et al., 2008). This experiment also got the result, but Al dissolution declined significantly with the increase of pH, indicating that there was no significant relationship between aluminum dissolution and total copper sorption amount. In previous studies we found that, with the pH declined, non-specific sorption rate increased significantly (Dong et al., 2006). This was further demonstration of Al dissolution by Cu^{2+} non-specific sorption.

2.2. Kinetics of Cu^{2+} sorption and Al dissolution

The kinetic curves of Cu^{2+} sorption by aggregates at 80 mg/L Cu^{2+} and 25°C were shown in Fig. 6. Sorption of Cu^{2+} increased rapidly at the beginning, and then became slow after 30 min. Therefore, the sorption process was divided into a fast (0–30 min) and a slow (≥ 30 min) sorption stages. The amount of Cu^{2+} sorbed at the fast stage accounted for 90%–95% of the Cu^{2+} total sorption capacity. This was similar to the previous results (Strawn and Sparks, 2000; Covelo et al., 2004; Roth et al., 2012). Our previous kinetics studies on Cu^{2+} sorption at different concentrations and temperatures showed that the specific sorption and non-specific sorption dominated at the fast and slow stages, respectively (Liu et al., 2015).

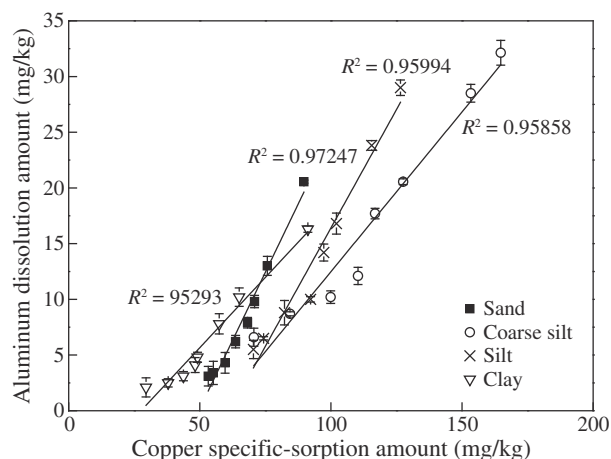


Fig. 5 – Relationship between Al dissolution and Cu^{2+} non-specific sorption at Cu^{2+} of 80 mg/L.

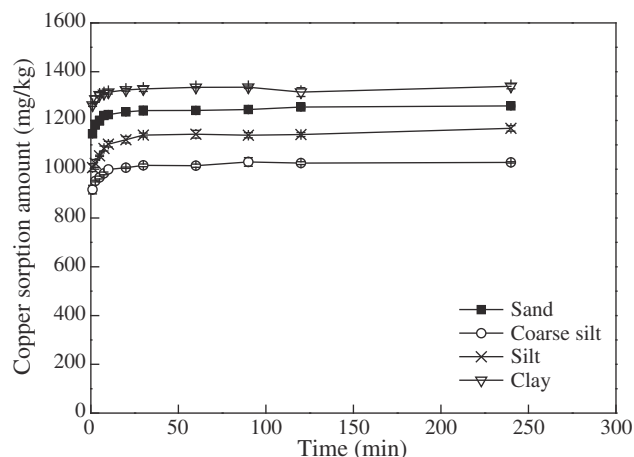


Fig. 6 – Kinetic curves of Cu^{2+} sorption by aggregates at pH = 5.5 and Cu^{2+} of 80 mg/L.

As showed in Fig. 7 the kinetic curves of Al dissolution under the same conditions as those of Cu^{2+} sorption. Similarly, Al dissolution curves could also be divided into two parts: fast and slow. However, Al dissolution at the fast stage was much slower than Cu^{2+} sorption. At the fast stage, the amount of Al dissolved within 90 min was about 80% of the total Al dissolution within 240 min. According to the theory of mineral complexation dissolution or acid dissolution, the sorption or dissolution rate of the exchangeable ions is fast; while the breaking of chemical bonds between metal ions and oxygen (O–M) and the dissociation of metal ions from solid surface into the solution are very slow. The reason for the two stages of Al dissolution rates is that soil aggregates contain Al solid phases with different stability (exchangeable Al, amorphous Al oxide, crystal Al oxide and kaolinite). Similar patterns have been observed in the research on Al releases from red soil by organic acids, in which the dissolution of exchangeable Al and amorphous Al oxide occurred at the rapid stage but that of crystal Al oxide and kaolinite happened at the slow stage (Li et al., 2006). However, further research on Al morphology after Cu^{2+} sorption is necessary.

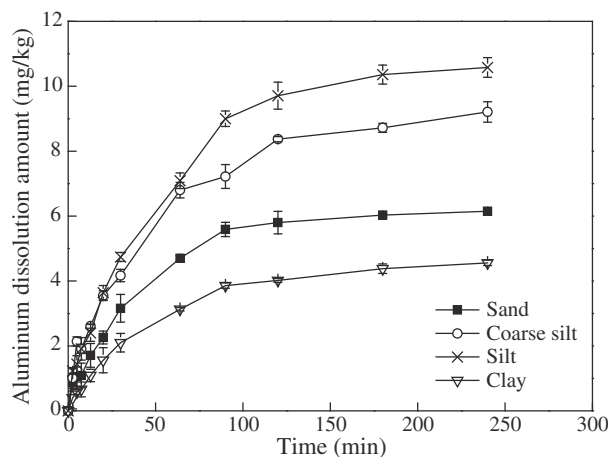


Fig. 7 – Kinetic curves of Al dissolution at pH = 5.5 and Cu^{2+} of 80 mg/L.

Table 2 – Progress (%) of Cu²⁺ sorption and Al dissolution.

Time (min)	Cu ²⁺ sorption				Al dissolution			
	Sand	Coarse silt	Silt	Clay	Sand	Coarse silt	Silt	Clay
0	0	0	0	0	0	0	0	0
2.5	76.8	85.9	87.8	86.1	11.4	8.8	12.5	11.0
5.0	78.4	87.6	88.7	86.7	13.3	12.7	15.0	23.2
7.5	79.5	88.4	89.2	87.4	17.7	14.5	15.6	20.7
10	83.2	89.7	90.2	87.3	22.2	23.9	24.5	28.3
20	89.2	91.4	92.1	88.6	33.7	34.2	32.4	38.5
30	93.5	95.3	93.4	90.6	43.9	46.1	45.3	45.3
60	94.6	96.0	94.1	93.8	65.6	68.6	67.3	73.8
90	95.2	96.2	95.1	94.1	83.3	84.6	80.1	78.4
120	95.7	97.4	97.3	95.2	89.9	88.2	83.1	86.5
180	97.8	99.1	97.8	97.6	97.8	91.7	92.1	94.7
240	100	100	100	100	100.0	100.0	100.0	100.0

To further investigate the mechanisms of Al dissolution during Cu²⁺ sorption, indexes of Cu²⁺ sorption progress and Al dissolution progress (the ratio of Cu²⁺ sorption (Al dissolution) at a time to the maximum Cu²⁺ sorption (total Al dissolution) at the equilibrium) were calculated (Table 2). The data showed that the Cu²⁺ sorption progress was significantly greater than the Al dissolution progress. At the 30th min, the former was more than 90%, while the latter only about 40%. The Al dissolution lagged behind the Cu²⁺ sorption. The results confirmed that Cu²⁺ specific sorption took place prior to non-specific sorption and Al dissolution occurred mainly at the non-specific sorption stage. Obviously, the relationship between and mechanisms of Cu²⁺ sorption and Al dissolution need further investigation.

3. Conclusions

- (1) Aluminum ion could be released only when Cu²⁺ sorption by aggregates was greater than a certain value. Aluminum dissolution increased significantly with increasing Cu²⁺ sorption and decreasing solution pH, and lagged behind the Cu²⁺ sorption. Aluminum dissolution mainly happened at non-specific sorption stage.
- (2) Soil solution pH decreased obviously after Cu²⁺ sorption by aggregates. The pH decline was positively correlated with Cu²⁺ sorption and Al dissolution. Smaller pH decline and Al dissolution in sand and clay fractions than coarse silt and silt fractions showed that sand and clay fractions had good inhibition and buffering effects on soil pH and Al dissolution and thus would play an important role in controlling soil acidification and Al toxicity. The present results imply that the soil environmental capacity for heavy metals may not secure soils. It is critical to pay attention to soil acidification and Al dissolution induced by heavy metal pollution.

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