Kinetics of soil cadmium desorption under simulated acid rain

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ABSTRACT

Soil acidification can result in the release of heavy metals stabilized by soil components into soil solution, and therefore it causes ecological risk. The kinetics of Cd desorption from two Chinese soils (ultisol and oxisol) distributed in the acid rain sensitive areas of southern China, were studied using a flow-stirred method under simulated acid rain conditions. Cd desorption was well described by the first-order kinetic equation. Percentages of Cd desorbed were 80–99% in ultisol and 25–28% in oxisol, respectively. Cd desorption, regarded as a heterogeneous diffusion in soils, could be also fitted by the Elovich equation. The desorption process could be divided into a fast reaction and a slow reaction, which were corresponded to the exchangeable and the specific sorbed Cd, respectively. The obtained results are essential to understand the process of heavy metal release under acid deposition conditions and to evaluate the ecological risk of acid deposition in those acid rain sensitive areas of China.

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1. Introduction

Large amounts of heavy metals have accumulated in agricultural soils in China due to industrialized development in rural and urban regions during recent decades. Among the heavy metals, cadmium (Cd) contaminated agricultural land received special attentions and increased quickly in recent years in China (Chen et al., 2000). Cd sources in agricultural fields were strongly affected by anthropogenic activities, such as industrial wastes, mine activities, irrigation by wastewater, application of sewage sludge and P fertilizers, and atmospheric deposition (Naidu et al., 1997; Chen et al., 2000).

The reactivity, mobility, bioavailability, and toxicity of Cd are strongly affected by sorption and desorption processes, which depend on the metal partitions between solid phases and the soil solution. The concentrations of heavy metals in soil solution are most likely governed by sorption and desorption of the heavy metal with different soil constituents, such as various hydrous oxides, clay minerals and organic matter (OM) (Ainsworth et al., 1994). Other factors such as soil pH, temperature, ionic strength and time could also play important roles in Cd sorption–desorption reactions (Ainsworth et al., 1994; Gray et al., 1998; Eick et al., 1999).

Previous studies indicated that Cd desorption was as important as its sorption. However, desorption behavior of a metal ion usually

differs from its sorption and lead to a lack of coincidence in the experimentally obtained sorption and desorption conditions (Shirvani et al., 2006). Desorption of heavy metals from solid surfaces is also strongly pH dependent, which is an important process regulating metal concentrations in soil solution. The desorption efficiency was greater than 80% for Ni(II), Cu(II), Zn(II) and Cd (II) on ferrihydrite in 30 min at pH 4.5 (Schultz et al., 1987). Cd release rates were very low at pH above 5.0 and increased exponentially as pH decreased below 4.5 for afforestation of cultivated soil (Strobel et al., 2001). Those results were mostly investigated by equilibrium techniques at different pH conditions. However, the kinetic processes of Cd desorption influenced by pH are still poorly understood in variable charged soils.

Acid rain is recognized as one of the major environmental issues in recent decades due to rapid economic development in China (Larssen et al., 1999). Some researchers reported that acid rain with pH from 3.0 to pH 4.5 usually occurred in large areas mainly south of the Yangtze River, especially in the suburbs of industrial cities (Wang and Ding, 1997). It caused deterioration of ecosystem and soil fertility in tropical and subtropical areas, such as accelerating soil acidification, resulting in the activation of aluminum (Al) and toxic heavy metals and thus increasing their ecological risk (Yu, 1997; Liao et al., 1998; Xu and Ji, 2001). However, the influence of acid rain on Cd desorption from the soils of the acid rain sensitive area in southern China received very limited attention.

Traditionally, desorption studies were performed using batch methods, which could not reflect naturally occurring processes due to leaching or plant uptake over time. The process of Cd desorption could be controlled mainly by time-dependent, rather

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than equilibrium reactions. In methodology, the flow technique combines some of the favorable aspects of both batch and miscible-displacement techniques (Bar-Tal et al., 1990). It reflects mechanisms and reaction rates of ionic nutrients in soils (Spark et al., 1995). The purpose of this study was to measure the rate parameters of Cd desorption kinetics by using an improved stirred-flow technique. The findings would improve understanding of Cd desorption mechanisms from variable charge soils by simulated acid rain in order to provide information for evaluation of Cd potential toxicity and ecological risk in acid rain areas of China.

2. Materials and methods

2.1. Soil samples

An oxisol (located at 110°10'E, 20°20'N, Xuwen, Guangdong province) and an ultisol (located at 116°56'E, 28°13'N, Yingtan, Jiangxi province) were collected from acid rain sensitive area in southern China. The samples were air-dried and passed through a 60-mesh sieve. The oxisol was derived from basalt and the dominant clay components were kaolinite and Al and iron (Fe) oxides. The ultisol was derived from the Quaternary red earth and the clay minerals included kaolinite, illite and vermiculite. Basic soil properties were pH(H₂O) 5.61, pH(KCl) 5.40, soil organic matter (SOM) 5.8 g/kg, clay content 640.0 g/kg and CEC_{pH7.0} 7.15 cmol/kg for the oxisol; and pH(H₂O) 4.57, pH(KCl) 3.81, SOM 9.1 g/kg, clay 515.4 g/kg and CEC_{pH7.0} 11.2 cmol/kg for the ultisol, respectively. The pH was determined in distilled water and in 1M KCl with a 1:2.5 soil:solution ratio, the clay contents by the pipette method, Fe oxides content (Fed) by dithionite citrate bicarbonate extraction, organic matter by the classical method of dichromate oxidation, and soil cation exchange capacity (CEC_{pH7.0}) by the conventional NH₄Ac method. The point of zero charge (ZPC) of the samples, by STPT method (Sakurai et al., 1989), was 4.42 for oxisol and 3.12 for ultisol. These two soils had high contents of clay and total Fe oxides, and low pH, low organic matter and low CEC, clearly identified as variable charge soils.

2.2. Simulated acid rain

SO₄²⁻ and NO₃⁻ in the acid rain of southern China were 90–140 and 26–70 μM from 1986 to 1993, respectively (Wang and Ding, 1997). According to this chemical composition of the rainfall in southern China, the simulated acid rains in this experiment were made of a H₂SO₄ to HNO₃ mole ratio of 4:1 with pH 3.5 and pH 4.5.

2.3. Cd sorption

Batch sorption studies were performed at 25 °C to obtain the equilibrium isotherms in triplicates. A series of 100 ml plastic centrifuge tubes were filled each with 50 ml of Cd solution of varying concentrations (0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mM) in 0.01 M KNO₃ background electrolyte with a 1:10 soil to solution ratio. The samples were added into each tubes and shaken for 2 h in a horizontal reciprocating shaker, left for 24 h. Supernatants were centrifuged for 10 min at 4500 rpm and filtrated with 0.45 μm filter paper. The residual soils were collected and rinsed with absolute alcohol. These samples were dried to be prepared to perform the kinetics of Cd desorption. The supernatants were analyzed for Cd by flame atomic absorption spectroscopy (AAS vario 6, Analytic Jena, Germany) and Cd concentration retained in the adsorbent phase (mmol/kg) was obtained. The sorption data were fitted to Langmuir and Freundlich equation (Harter and Baker, 1977; Sposito, 1980).

2.4. Kinetics of Cd desorption

A continuous-flow-stirred reactor technique, modified from Shiohatana et al. (2001), was used to determine the kinetics of Cd desorption under acidic solution. The basic components of this kinetic device included acidic solution, peristaltic pump, magnetic stirrer, flow-stirred reactor and fraction collectors as shown in Fig. 1.

Cd desorption was carried out using above sorbed Cd samples. Each treatment of desorption kinetics was coded by according to effluent pH and added Cd concentrations (mM) in equilibrium experiment, such as pH4.5 (0.6). Each 1.0 g of soil samples by Cd sorbed was placed into the reactor and then assembled the pieces of the device. All experiments were controlled at 25 °C in duplicate. The simulated acid rain was passed through a silicone tube of 2-mm in inner diameter into the reactor to sufficiently mix with samples using a peristaltic pump. The reactor and its cover were made of organic glass to have a capacity of approximately 10 ml. The outlet of the reactor was furnished at upside with a filter (0.45 μm microfibre filter, 30 mm in diameter) to allow solution to automatically flow through at inner pressure with 1.0 ml/min flow rate. The effluent was collected in constant volume with an auto-digital control fraction collector at designed-made time when the first drop flowed out. Influent volume was collected. Cd concentration and pH of the effluent were analyzed.

3. Results

3.1. The equilibrium concentrations and the amounts of Cd sorption

The amounts of Cd sorbed in the soils increased with increasing Cd concentrations in the equilibrium solution. The corresponding parameters were modeled by the Langmuir and Freundlich equations, which the determination coefficients (*R*²) were 0.922 and 0.998, respectively.

Based on the Langmuir equation, the maximum sorption capacity (*Q*⁰) was 9.23 and 3.67 mmol/kg for the oxisol and ultisol, respectively. The corresponding *b* values, related to the free energy of sorption and the affinity of the binding sites, were 0.108 and 0.324 l/mmol, respectively. Unlike the Langmuir model, the differences in sorption enthalpy between different types of sites were accounted for by the Freundlich model. *K_f* values, the relative sorption capacity for Cd, were 9.46 and 3.06 mmol/kg for the oxisol and ultisol, respectively. 1/*n* values, the surface affinity to Cd had the obvious difference from the energy sites of Cd sorption, were 0.439 and 0.509 for the oxisol and ultisol, respectively. The relative sorption capacity had the same order as *Q*⁰ value. The difference of amounts of sorbed Cd could be related to the different pH at the equilibrium in the soils. The solution pH values at equilibrium were from pH 5.6 to pH 5.2 in the oxisol and from pH 4.8 to pH 4.4 in the ultisol with added Cd concentrations, respectively. The

Fig. 1. Sketch of a continuous-flow-stirred kinetic device used in this study.

Fig. 2. The relationship between the concentrations vs. the time for Cd desorption from the ultisol and oxisol.

percentage of Cd sorption was about 60–70% in the oxisol and 25–30% in the ultisol at high Cd concentrations. The different pH values at equilibrium solution could reflect the species of sorbed Cd onto solid surface.

3.2. The reactive time and the concentrations of Cd desorption

The effluent volume was invariably collected at 1.0 ml/min of the velocity of flow using automatic collector in this experiment. It could be reflected that the concentration of Cd desorption changed with the time. The effluent concentrations of Cd decreased sharply during 0–60 min as shown in Fig. 2. The experimental data showed that the concentrations of Cd desorption are different from between the capacity of sorbed Cd and the influent pH. The amounts of desorbed Cd were 36.5, 49.9, 66.8 and 94.4 μM for pH4.5 (0.6), pH4.5 (1.0), pH3.5 (0.6) and pH3.5 (1.0) treatments in the ultisol, 16.8 and 44.3 μM for pH4.5 (0.8) and pH3.5 (0.8) treatments in the oxisol during 0–10 min, and then dropped to 5–10 μM at 60 min. It could be shown further that the desorption process nearly completed during 0–60 min in the obvious fast reaction stage, and then closed to pseudo-equilibrium state. Therefore, the kinetics of Cd desorption from the soil surface had two clear stages: a very rapid stage during 0–60 min and then a very slow stage.

3.3. Effluent pH change during Cd desorption process

The effluent pH changes in Cd desorption process was shown in Fig. 3. As to the influent pH 3.5, the effluent pH decreased from pH 4.2 moderately down to pH 3.7 in 80 min in the ultisol, and fluctuated at pH 6.0 in the oxisol. As to the influent pH 4.5, the effluent pH fluctuated at pH 5.0 in the ultisol, and increased from

pH 6.2 up to pH 7.2 in 40 min and then decreased to pH 6.5 in the oxisol. This results indicated that it had a great quantity of H^+ consumption in the two soils during the desorption process. It was observed that the effluent pH values were above 7.0 in the oxisol, which could be deduced that OH^- released from the soils during the process of Cd desorption. It was also noted that H^+ consumption could have the fast reactive process in 80 min and followed by the slow reaction for pH 3.5 in the ultisol.

3.4. The kinetic equations of Cd desorption

The accumulative amounts of Cd desorption were calculated according to influent volume and Cd concentration. Several kinetics were used to fit the relationship between desorbed amounts and time, such as

$$\text{the first order kinetics : } \ln\left(1 - \frac{q_t}{q_\infty}\right) = -k't \quad (1)$$

$$\text{Elovich equation : } q_t = a + b \ln t \quad (2)$$

where q_t is the amount desorbed in any time, q_∞ is the maximum amount desorbed, t is time, a and b are the parameters of the equations. The major parameters of kinetics were in Table 1.

By using the first-order kinetics to fit the data of Cd desorption, the determination coefficient (R^2) was more than 0.99. The average value of k' increased from 0.013 to 0.023 in the oxisol and from 0.021 to 0.056 in the ultisol as the influent pH decreased from pH 4.5 to pH 3.5, respectively. The k' value increased with an increase in the effluent acidity, which implied the solution acidity enhanced the rate of Cd desorption. The bigger the k' value was, the quicker the fast reactive stage was. In order to compare the

Fig. 3. Change of effluent pH in Cd desorption process from the ultisol and oxisol.

Table 1

Major parameters of the kinetics of Cd desorption from two soils.

Soils	Treatment code	q_e	$(q_\infty/q_e) \times 100$	The first-order kinetics, $\ln(1 - q_t/q_\infty) = k't$			Elovich equation, $q_t = a + b \ln t$	
				q_∞	k'	R^2	b	R^2
Ultisol	pH4.5(0.6)	1.97	84.3	1.66	0.021	0.992	0.46	0.994
	pH4.5(1.0)	2.84	75.7	2.15	0.020	0.992	0.57	0.995
	pH3.5(0.6)	1.97	99.0	1.95	0.056	0.996	0.77	0.996
	pH3.5(1.0)	2.84	99.6	2.83	0.048	0.998	1.08	0.999
Oxisol	pH4.5(0.8)	5.62	25.2	1.40	0.013	0.998	0.41	0.980
	pH3.5(0.8)	5.62	28.1	1.58	0.023	0.966	0.43	0.972

Where R^2 for coefficient of determination, t for time (min), q_t for amounts of desorption (mmol/kg) at t time, q_∞ for the maximum amounts of desorption (mmol/kg), q_e for amounts of adsorption (mmol/kg) at equilibrium. Each treatment was coded in according to the effluent pH and added Cd^{2+} concentrations at equilibrium sorption, such as pH4.5 (0.6).

efficiency of Cd desorption by the simulated acid rain from the soils, the percentage of Cd desorption was defined as the ratio of the theoretical desorption amounts and actual sorption amounts. The percentage of Cd desorption increased from 80% to 99% in the ultisol and from 25% to 28% in the oxisol as the influent pH from pH 4.5 to pH 3.5, respectively. It implied that Cd desorption was nearly completely reversible in the ultisol, but mostly not reversible in the oxisol.

In this experiment, the data by fitting Elovich equation indicated that the relationship between q and $\ln t$ was expressed by two linear equations, which was consistent with the fast reaction and the slow reaction of Cd desorption. The determining coefficient (R^2) of the linear equation was 0.972–0.998 in the fast reaction. From the Elovich equation, the rate equation at Cd releasing was obtained by $dq/dt = b/t$. The b value was used to compare the relative rate of Cd releasing and was relative to the diffusion rate of Cd from solid phase to the bulk solution. The b values in the fast reactive stage averaged 0.51 and 0.92 for pH 4.5 and pH 3.5 in the ultisol, 0.32 and 0.34 for pH4.5 (0.8) and pH3.5 (0.8) in the oxisol. The bigger the b value was, the faster the relative rate of Cd diffusion was.

4. Discussion

4.1. The meaning of kinetics of Cd desorption in the soils

In the equilibrium sorption experiments, the species of Cd in solution had made an influence on the speciation of Cd in solid phase which was relative to the degree of Cd desorption. The distribution of Cd species in solution were Cd^{2+} , $\text{Cd}(\text{OH})^+$ at $\text{pH} < 6.0$ and Cd^{2+} , $\text{Cd}(\text{OH})^+$, $\text{Cd}(\text{OH})_2$ at $\text{pH} 6.0\text{--}7.0$ according to a function of pH in the solution. The sorption reactions at the solid phase interface involved interaction with deprotonated surface hydroxyl groups to form inner- and outer-sphere complexes which the pH_{zpc} value was considered (Schindler et al., 1987; Randall et al., 1999). Firstly, acid–base reactions at the mineral surface can be expressed as

The selected oxisol and ultisol, called as variable charge soils, were distributed widely in the vast tropical and subtropical regions of southern China. As the solution pH at the equilibrium sorption of Cd was above the pH_{zpc} of soils, the surface reactions of Cd sorption were assumed to form SOCd^+ , $\text{SOH} \cdots \text{Cd}$ and $(\text{X}_2)^{2-} \cdots \text{Cd}^{2+}$.

Where SOH , SOH_2^+ and SO^- represent a neutral, protonated and deprotonated surface sites respectively, and X^- represents a permanent negatively charged site. SOCd^+ depicts the formation of an inner-sphere Cd surface complex, while $\text{SOH} \cdots \text{Cd}$ and $(\text{X}_2)^{2-} \cdots \text{Cd}^{2+}$ represent the formation of outer-sphere surface complexes.

Gunneriusson (1994) thought that $\text{SOH} \cdots \text{Cd}^{2+}$ was the major sorbed species below pH 6, SOCd^+ dominated at pH 6–8. From pH values at equilibrium sorption, the species of Cd sorbed could be mainly SOCd^+ , $\text{SOH} \cdots \text{Cd}^{2+}$ and $(\text{X}_2)^{2-} \cdots \text{Cd}^{2+}$ in the oxisol and ultisol. At low pH, H^+ could successfully exchange Cd from sites of $\text{SOH} \cdots \text{Cd}^{2+}$ and $(\text{X}_2)^{2-} \cdots \text{Cd}^{2+}$. By the experimental results, it may be reasoned that the easily desorbed Cd could be $\text{SOH} \cdots \text{Cd}^{2+}$ and $(\text{X}_2)^{2-} \cdots \text{Cd}^{2+}$, and the difficulty sorbed Cd could be SOCd^+ in the form of the inner-sphere complexation.

The kinetic curves of Cd desorption can be divided into two stages in the acidic solution. The first stage located within the initial 60 min, at which the release rate of Cd was very fast and the released Cd dominantly originated from exchangeable $\text{SOH} \cdots \text{Cd}^{2+}$ and $(\text{X}_2)^{2-} \cdots \text{Cd}^{2+}$. The slow stage was from specific sorption of SOCd^+ . Sparks (1987) reported the suitability of the Elovich equation to describe the diffusion mechanism of slow reaction and it could explain various energetics of the chemisorption. The heterogeneous active sites in surface exhibited different activation energies for chemisorption (Teng and Hsieh, 1999). Taylor et al. (1995) successfully applied the Elovich equation to the sorption of zinc ions in soils. Juang and Chen (1997) also used the Elovich equation in the sorption of metals on solvent impregnated resins. Our results indicated that energetic distributions of surface were heterogeneous, which were consistent with equilibrium isotherm of Cd sorption by using the Freundlich equation. It indicated that the process of Cd desorption could be controlled by the different rate mechanisms involving in the system pH.

4.2. The influence of pH on Cd desorption

The rate of Cd desorption increased with a decrease of the influent pH value from 4.5 to 3.5 by the estimations of the rate constants (k' and b values). H^+ ion could be sorbed in the bonding sites of mineral surface, which will lead to the increasing amount of Cd desorption, such as following reactions:

The different affinity of the bonding sites to Cd may cause the difference in the rates and amounts of Cd desorbed. Furthermore, the surface protonation in soils promoted dissolution of Fe in acid solution to increase Cd desorption (Eq. (7)):

The Cd desorption in the ultisol and oxisol could be dependent on the composition of the clay minerals, pH and anion ions of acid solution. While releasing kinetics of metals were governed by environmental conditions such as pH, the effluent pH, about 6.0–7.3 in oxisol and about 3.5–5.0 in ultisol, will also have an influence

on Cd desorption. It indicates the consuming processes of H^+ in the oxisol differed from that in the ultisol. H^+ ion consumption is an important factor which affects the solution pH. Firstly H^+ ions could only exchange some metal cations, but the surface hydroxyl groups attached to Fe or Al atoms could accept protons from solution, resulting in an increase in positive surface charges, called as the protonation in mineral surface (Zhang et al., 1991; Zhu et al., 2005). The protonation is a very fast reaction at the initial stage and depended on the amounts and properties of Fe-OH. Secondly, the specific adsorption of SO_4^{2-} on the surface of the minerals could release OH^- for neutralizing H^+ in the solution. This mainly depends on the content of ferric oxides in the two soils (Yu, 1997). The mechanism was as follows:

The obvious difference of surface properties between in the oxisol and in the ultisol has different influence on Cd desorption in short time under simulated acid rain containing SO_4^{2-} . If OH^- release and surface protonation were very fast, it could consume a large quantity of H^+ to decrease the amounts of Cd desorption.

4.3. Cd desorption and ecological risk

The bioavailability, toxicity and mobility of heavy metals in soils are largely determined by their kinetic processes between solution and solid phases. Factors such as pH may play a dominant role in controlling the nature of the interactions between metals and the soil surfaces (Zhang et al., 2006). The rates of metal release from the solid phase provide the basic information for describing the kinetic processes.

This research shows that Cd releases so quickly from the solid phase to the solution. The k' and b values increased about one time for pH 3.5 more than for pH 4.5 in the ultisol. The effluent pH values were 4.2–5.0 and the percentage of Cd desorption was 80–99%. Cd sorption–desorption process is approximately reversible by the influence of the solution pH. As the soil pH decreases, metals are desorbed from soil particles, and enter the soil solution and become more mobile (Li and Wu, 1999). In the oxisol, the slightly faster rates of release were observed. The effluent pH values were 6.0–7.2, and the percentage of Cd desorption was 25–28%. As compared to other toxic heavy metals, Cd is exceptionally soluble in soil. Cd is relatively mobile between the pH of 4.2 and 6.6, and only moderately mobile between the pH of 6.7 and 8.8 (Schmitt and Sticher, 1991). Below pH 5, dissolved Cd concentration increased rapidly due to pH dependent desorption from the soil surface. As for a soil, fluxes of metals from the stirred chamber are similar to fluxes to plants. Rates of metal release from the solid phase may limit the rate of Cd supply to plants in these soils. The soluble capacity of toxic metals will significantly increase if the soil solution is acidified by acid rain. The potential threat of Cd under acid rain conditions should receive attention in the acid rain sensitive areas of China.

5. Conclusion

The processes of Cd desorption from the ultisol and oxisol consisted of a fast reaction and a slow reaction, which were corresponded to exchangeable and specific Cd adsorption, respectively. As the energy distributions of sites of sorption in the soils were heterogeneous, the bonding sites of edge hydroxyl had the different affinity to the sorbed Cd, which led to the difference of the rate and amount of Cd desorption. Cd desorption could be well described by the first-order kinetics and Elvoich equation. The different mechanisms of Cd sorption–desorption could be related to the solution pH and the properties

of the soils. The increase of effluent pH reflected the different ways of H^+ consumption which exchanged with metal ions, increased the positive charge as protonation, and neutralized OH^- released by the specific sorption of SO_4^{2-} in the acid rain. Cd release under simulated acid rain could significantly increase its ecological risk.

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