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Adsorption characteristics of Cu and Zn onto various size fractions of aggregates from red paddy soil

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HIGHLIGHTS

- The clay-size aggregate showed faster adsorption rate and larger capacity.
- pH effect the adsorption and desorption of various aggregates at different levels.
- The clay-size aggregate may accumulate metals more easily in natural environment.
- Metal speciation in the clay-size aggregates appeared to be more stable.

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ABSTRACT

Soil aggregate is the basic structure unit of soils and the ability of various size fractions are different in the aspect of adsorbing and transferring heavy metals in the environment. In this study, bulk soil from red paddy field was partitioned into four aggregate-size fractions and their adsorption characteristics for Cu and Zn were studied. Our results showed that: Pseudo-second order model was more successful to fit the adsorption process in the kinetic experiments and the isothermal experiments data can be described well with the Freundlich model as a whole. Due to higher contents in organic matter, CEC and free iron oxide, the <0.002 mm fraction was found to have the highest initial sorption rate and maximum adsorption capacity. The adsorption amount of metals increased as the increasing of pH and the percentage of adsorbed metal susceptible to desorption into 0.01 M $NaNO_3$ was greater for Zn than for Cu, while their variation trends were quite opposite. More specific adsorption sites in the <0.002 mm fraction lead to more desorption amount for this particle size of soil at low pH condition. After 60 days of incubation, Cu and Zn were observed to enrich in the clay-size aggregates with fractions more stable than other particles.

1. Introduction

Heavy metal pollutants in the environment mainly come from anthropogenic industrial and agriculture activities, they can enter soil system in different ways such as atmospheric sedimentation, waste water irrigation and slag leaching etc. [1]. Past researches have shown that potential mobility of metals in soils was mainly determined by adsorption–desorption process [2]. Through adsorption, heavy metals only accumulate in top-soils in the case of relative low concentration, however, they will migrate to deep soil layers and further contaminate groundwater by rainwater leaching or irrigation when pollution level exceed a certain extent. Metals retained in the top-soils will not only be a potential hazard to plants, animals and micro-organisms, but finally pose a great threat to human health through the food chain [3–5].

As the basic structural unit of soil, aggregate has been long used to investigate the distribution and migration of organic matter and nutrients in soils [6,7]. Due to different physical–chemical characteristics, the ability of various particle size aggregates in adsorbing foreign materials (metals, N, P, etc.) may be different and it is commonly believe that fine soil particles have a higher ability to carry heavy metals than coarser particles because of lager specific surface area and more organic matter, Fe/Mn/Al oxides contents [8–12]. Furthermore, fine soil fractions are often preferentially to transport to deep soil, surface/ground water and air [13,14]. Therefore, it is very necessary to study the adsorption process between heavy metals and soil aggregates of different size fractions to evaluate associated environmental risk. Up to date, although some related studies have done [7,15–17], most of the them were carried out

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Abbreviations: V/V, volume per volume; AF_x, accumulation factor.

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with the subjects of urban soil [8], dust [18] and sediment [19], while arable soil has been neglected. In addition, these studies were mostly focused on the distribution of metals in polluted soils, adsorption properties and relative influence factors have not been evaluated.

The major factors controlling adsorption process include metal speciation and strength, soil type, pH, contact time and temperature, etc., among which pH is considered as the most significant environmental factor due to its strong effects on solubility and speciation of metals both in the soil as a whole and particularly in the soil solution [20]. Usually, the adsorption capacity of heavy metal is positive correlated to soil pH, in other words, low pH means metal ions are more likely to exist in soil solution and consequently more easily to migrate and uptake by plants [21]. In south China, overuse of fertilizer has contributed substantially to croplands soil acidification since the 1980s [22], meanwhile, part of the agricultural soil has suffered serious heavy metal pollution. This situation has result in over-standard concentrations of heavy metals in surface water, groundwater and crops [23], so it is make sense to study the effect of pH on the adsorption–desorption of metals with the objects of soil aggregates in this area.

In this paper, we investigated the adsorption characteristics of Cu and Zn onto various red paddy soil aggregates by kinetics, thermodynamics and pH effect experiments. Moreover, an incubation experiment was conducted to simulate heavy metal pollution in soil close to the natural conditions, and metal speciation in different size fractions was analyzed. By analyzing all the data from the experiments above, it is hope to gain an insight into the adsorption mechanism between soil and heavy metals and assess pollution risk of heavy metals in soil more reasonably.

2. Materials and methods

2.1. Soil samples and aggregates fractionation

The soil samples used in this paper were collected from a paddy field, 15 km away from the center of Changsha city in Hunan province. The agrotype is a typical red paddy soil widely distributed in southern China. Previous research in this area showed there was no significant heavy metal pollution in the soil. Five sample sites were selected and approximately 0.5 kg soil in each site was collected from the surface layer (0–20 cm). After mixing, all the bulk samples were air dried at room temperature, roots and other large particles were removed, then ground and sieved through a 2 mm nylon screen.

The samples were partitioned into four aggregate-size fractions: 2–0.25 mm, 0.25–0.05, 0.05–0.002 and <0.002 mm. Before fractionation, 30 g of bulk soil was immersed in 150 ml deionized water (in a conical flask, 250 ml) and dispersed with ultrasonic. The ultrasonic energy was set to 100 J/ml according to Schmidt et al. [24] who suggested that dispersion with energy in the range 30–590 J/ml revealed no evidence for detachment and redistribution of organic matter. Then the 2–0.25 mm fraction was obtained by wet sieving, the 0.25–0.05 and 0.05–0.002 mm fractions were obtained by sedimentation and siphoning, during times determined by Stokes' law. The <0.002 mm fraction was finally obtained after centrifuging. All the soil particles of four size fractions were collected respectively and freeze-dried for later experiments.

2.2. Kinetics adsorption experiments

Bulk soil or different aggregate fraction sample (3 g) was placed into a 250 ml conical flask, 150 ml 0.01 M $NaNO_3$ solution containing 100 mg/l Cu (as $Cu(NO_3)_2$) or Zn (as $Zn(NO_3)_2$) was then added. The suspensions were shaken at 160 rpm at a constant temperature of $25 \pm 0.2\,^{\circ}C$. A volume of 5 ml mixture was extracted by syringe, filtered through 0.22 μm micro membrane, at different periods of time (5, 10, 20, 30, 40 min, 1, 2, 4 and 8 h), and then the concentration of heavy metal was measured. Amount of metals removed from the solutions by the soil was calculated from the decrease of metal-concentration in the solutions.

Pseudo-first order kinetic [25] and pseudo-second order [26] kinetic equations were applied to fit the data from the kinetic studies, Eqs. (1) and (2):

$$lg(q_e - q_t) = lg(q_e) - \frac{k_1}{2.303}t \qquad (1)$$

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

where k_1 (/min) and k_2 (g/(mg min)) are the rate constants of adsorption; q_e and q_t (mg/g) are the amounts of solute adsorbed per unit adsorbent at equilibrium and at time t, respectively. The initial adsorption rate v_0 (mg/(g min)) is calculated as $v_0 = k_2 q_e^2$.

2.3. Isothermal adsorption experiments

Isotherm adsorption experiments were performed with the following procedures: 0.5 g of bulk soil or aggregates of different size fraction was placed into a 50 ml polypropylene centrifuge tube, 25 ml 0.01 M $NaNO_3$ solution containing a series concentration levels (1, 5, 10, 20, 50, 100, 200, 500 mg/l) of Cu (as $Cu(NO_3)_2$) or Zn (as $Zn(NO_3)_2$) was add to each tube. The suspensions were shaken at 160 rpm for 4.0 h and then kept still for 20.0 h at a constant temperature of $25 \pm 0.2\,^{\circ}C$. At the end of each adsorption period, the suspensions were centrifuged at 4000 r/min for 20 min and supernatants were filtrated for measurement of metal concentrations.

Langmuir and Freundlich equations [27] were applied to fit the data from the isotherm studies, Eqs. (3) and (4):

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \qquad (3)$$

$$q_e = K_F {C_e}^{1/n} \qquad (4)$$

where q_e is the amount of adsorbed metal concentration at equilibrium (mg/kg); C_e is the concentration of the metal in solution at equilibrium (mg/l); q_m is the maximum adsorption amount of metal on soil (mg/kg); and K_L (l/kg), K_F (l/kg) and $1/n$ are constants.

2.4. Adsorption and desorption at different pH

The adsorption characteristics of Cu and Zn ions at a pH range of 2–6.5 were studied. 0.5 g bulk soil or aggregates of different size fraction was placed into a 50 ml polypropylene centrifuge tube, 25 ml 0.01 M $NaNO_3$ solution containing 100 mg/l Cu (as $Cu(NO_3)_2$) or Zn (as $Zn(NO_3)_2$) were added to each tube. The pH of the solution was adjusted to 2, 3.5, 5, and 6.5 respectively by adding HNO_3 and NaOH solution. Suspensions were shaken and centrifuged as in the isotherm adsorption experiments, the supernatants were poured out and filtrated for measuring pH and concentrations of heavy metals. Afterwards, 25 ml 0.01 M $NaNO_3$ was added to each tube to replace the adsorbed heavy metals in centrifuged residue, the followed procedures (shaken, equilibration, centrifugation and separation) were the same as in the previous experiments. Total desorption capacities of the adsorbed Cu and Zn were obtained by repeating this sequence of operations for three times.

2.5. Incubation experiment

Incubation experiment was conducted with 450 g soil in 500 ml beakers. Amount of 200 mg/kg Cu or 500 mg/kg Zn was added

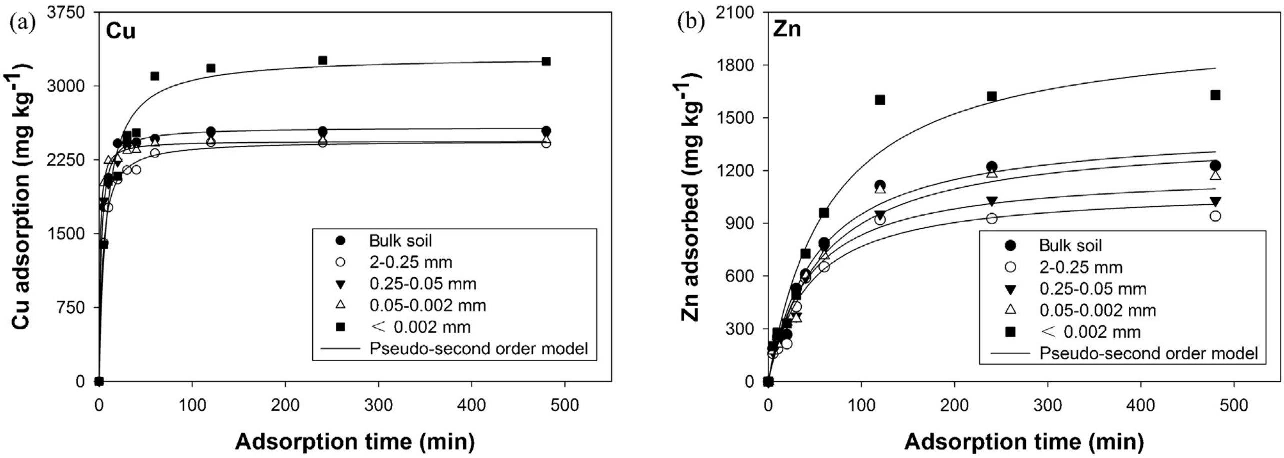

Fig. 1. Adsorption kinetics of Cu (a) and Zn (b) onto bulk soil and aggregates, the experimental data are reported as points and pseudo-second order model by curves.

as $Cu(NO_3)_2$ or $Zn(NO_3)_2$ solution (pH was adjusted to 6 ± 0.1 which is close to the actual pH of soil) to the beaker and then mixed with soil thoroughly. The different adding concentrations of the two metals were chose based on their background values and Chinese Environmental quality standard for soils [28]. The soil was maintained at about 70% of water holding capacity by weighing the beaker and adjusting the weight by addition of deionized water. The samples were incubated for 60 d in a thermostatic-humidistat incubator at 25 °C. After incubation, the soil was air dried again, partitioned to different aggregate size fractions with the method described above. Metal contents in bulk soil and aggregates were determined after HNO_3–HF–$HClO_4$ digestion. In addition, fractionation of heavy metal was determined by the sequential extraction procedure of BCR method. Details of the procedure can be found in relevant literature [29].

2.6. Physical and chemical analysis of the soil particle

Soil pH was measured in deionized water at a soil/solution ratio of 1:2.5 using HI 3221 pH meter (Hanna instruments inc., USA). Soil organic carbon (SOC) was determined by $K_2Cr_2O_7$ digestion method [30]. Cation exchange capacity (CEC) was determined by $BaCl_2$ displaced method [31], free iron oxide was determined by $Na_2S_2O_4$–$Na_3C_6O_7$ extraction method [32]. Total metal content in soil was determined by TAS-990 flame atom adsorption spectrophotometer (Persee inc., China) after HNO_3–HF–$HClO_4$ digestion process. Some basic properties of soil are presented in Table 1. All the glassware used in experiments were thoroughly rinsed with deionized water and soaked overnight in a 10% (V/V) HNO_3 solution. All experimental data were the average of triplicate determinations and coefficients of variation were less than 6% in all cases. Statistical analyses were conducted using SPSS 10.0 software.

3. Results and discussion

3.1. Adsorption kinetics

Results of the kinetic experiments are shown in Fig. 1(a) and (b), respectively, the adsorption amounts increased remarkably in the first 60 min for Cu and Zn, which accounted for over 95% Cu and approximately 65% Zn on average of total amounts of metals adsorbed within 8 h, respectively. Then the adsorption rate decreased gradually until adsorption equilibrium was obtained. Possible reason for this phenomenon was that there were enough binding sites for metals on the external surface of soil particles at the initial period, so the reaction was fast, then with the saturation of the binding sites, slow intraparticle diffusion occurred and was gradually dominant [33]. Parameters of adsorption kinetics for Cu and Zn were calculated from experimental data using Eqs. (1) and (2) (Table 2).

The calculated R^2 indicate that the pseudo-second order kinetic equation is more successful to fit the adsorption process of Cu ($0.9729 \leq R^2 \leq 0.9994$), while the fitting result of pseudo-first order kinetic equation is relative poor ($0.9238 \leq R^2 \leq 0.9900$). For Zn, values of R^2 ($0.9761 \leq R^2 \leq 0.9867$, $0.9516 \leq R^2 \leq 0.9750$, respectively) for the both equations are roughly equivalent. Successful fitting of data with the pseudo-second order kinetic model suggests chemisorption of these two metals was the rate-controlling step [26]. It can be observed that the data points of the <0.002 mm fraction located at inflection point are not fit by the pseudo-second order kinetic equation (actually, similar phenomenon was also observed in the adsorption process of Zn). The possible reason was that special physicochemical properties (high specific surface area, chemical and mechanical stability, layered structure, high cation exchange, etc.) of the clay-size particles made the actual adsorption process inconformity with the assumptions of the pseudo-second order model [34]. Due to faster adsorption rate, the slow adsorption stage of the <0.002 mm fraction appeared earlier compared with other fractions which lead to weak fit for data

Table 1
Physicochemical properties of bulk soil and various size fractions of aggregates.

Particle size (mm)	SOC (g/kg)	CEC (cmol(+)/kg)	Free iron oxide (g/kg)	Cu (mg/kg)	Zn (mg/kg)	(%)
Bulk soil	56.37	41.23	11.97	24.66	62.73	–
2–0.25	54.62	43.16	12.03	29.52	72.72	10.07
0.25–0.05	49.84	39.93	10.86	22.32	55.15	23.45
0.05–0.002	50.00	40.35	12.22	23.67	52.86	49.68
<0.002	65.30	51.05	27.95	29.88	96.83	16.80

SOC: soil organic carbon; CEC: cation exchange capacity; %: mass percentage.

Table 2
Pseudo-first and pseudo-second order model parameters, R-squared values and initial sorption rates calculated from kinetics experiment data of Cu and Zn.

Particle size mm	Pesudo first-order equation			Pesudo second-order equation			
	q_e (mg/g)	k_1 ($\times 10^{-3}$/min)	R^2	q_e (mg/g)	k_2 ($\times 10^{-3}$ g/(mg min))	ν_0 ($\times 10^{-3}$ mg/(g min))	R^2
Cu adsorption							
Bulk soil	2.476	224.60	0.9900	2.581	0.1731	1.1528	0.9970
2–0.25	2.295	161.23	0.9700	2.444	0.1070	0.6393	0.9970
0.25–0.05	2.412	244.11	0.9760	2.518	0.1890	1.1985	0.9970
0.05–0.002	2.378	361.43	0.9834	2.440	0.1928	1.1421	0.9990
<0.002	2.974	80.67	0.9238	3.155	0.121	1.2080	0.9730
Zn adsorption							
Bulk soil	1.241	17.32	0.9867	1.448	0.0133	0.0278	0.9750
2–0.25	0.954	20.35	0.9775	1.099	0.0211	0.0255	0.9586
0.25–0.05	1.039	19.96	0.9849	1.196	0.0192	0.0275	0.9719
0.05–0.002	1.198	16.19	0.9834	1.406	0.0126	0.0248	0.9674
<0.002	1.697	14.59	0.9761	2.029	0.0074	0.0305	0.9516

points located at inflection point. The initial sorption rates (ν_0) of Cu (0.6393–1.2080 × 10^{-3} mg/(g min)) were much higher than that of Zn (0.0248–0.0305 × 10^{-3} mg/(g min)) and the clay-size fraction (<0.002 mm), compared with other fractions, had the highest value of ν_0 for both Cu and Zn. As a whole, ν_0 increased with the decrease of particle size except for the 0.05–0.002 mm fraction. This means that particle size is not the only factor influencing the initial adsorption rate, but rather integrated effect resulted from various physical–chemical properties of soil. The fastest adsorption rate observed in the < 0.002 mm fraction, considering from the calculation process of ν_0 in the pseudo-second order kinetic equations, could be due to the largest adsorption capacity in addition to larger specific surface area of this fraction.

3.2. Adsorption isotherms

Experimental data and adsorption isotherms for Cu and Zn adsorption onto bulk soil and aggregates are shown in Fig. 2(a) and (b), respectively. From these isotherm curves, adsorption amounts of Cu and Zn increased almost linearly at low equilibrium concentration range (virtually, Cu and Zn were almost completely adsorbed) and tend to flat at high equilibrium concentrations. At initial concentrations approximately higher than 50 mg/l, the adsorption affinity of Cu gradually increased moving toward an adsorption maximum, while the trend for Zn was observed at the initial concentration higher than around 20 mg/l, which could be explained by the fact that saturation of the studied soil was reached at a relative low concentration in adsorbing Zn.

Table 3 presents Langmuir and Freundlich isotherm parameters obtained and the R^2 values ranged from 0.9203 to 0.9720 and 0.9101 to 0.9663 for Cu, respectively, suggesting that both of the two models well describe the adsorption characteristics of the two metals, whereas for Zn, the fitting accuracy of Freundlich model ($0.9285 \leq R^2 \leq 0.9974$) is better than Langmuir model ($0.7895 \leq R^2 \leq 0.9409$). As listed in Table 3, the maximum adsorption capacity (q_m, calculated from the Langmuir equation) of Cu (4169.84–6230.10 mg/kg) are greater than that of Zn (1438.06–3205.27 mg/kg). The soil appeared to have a higher affinity for Cu which is consistent with many other studies [35–38]. For the various soil particles, the q_m of Cu decreased in the order: (<0.002 mm) bulk soil > 0.25–0.05 mm > 0.05–0.002 mm > 2–0.25 mm, and for Zn, the order followed: (<0.002 mm) > bulk soil > 0.05–0.002 mm > 0.25–0.05 mm > 2–0.25 mm. The q_m value of the < 0.002 fraction was 1.14–1.49 (Cu) and 1.45–2.22 (Zn) times than that of other fractions, respectively. This result is in agreement with some previous reports [8–10], finding that the clay particles (<0.002 mm) retain more heavy metals than coarser particles due to high surface areas and negative charges associated with fine particles especially on several types of claying minerals and organic matter. It is also showed the q_m values are not completely increase as the decrease of the soil particle size and the reason is that soil physical–chemical characteristics govern the adsorption phenomena beside particle size.

The relationship between soil characteristics as SOC, CEC and free Fe_2O_3 and q_m can be described using liner regression analysis (Table 4). The q_m is positively with SOC, CEC and free Fe_2O_3 content ($b > 0$). Moreover, among the three characteristics, SOC (Cu: $R^2 = 0.7401, P = 0.0389$; Zn: $R^2 = 0.8730, P = 0.0129$) is a more important factor in determining the adsorption capacity of soil particles

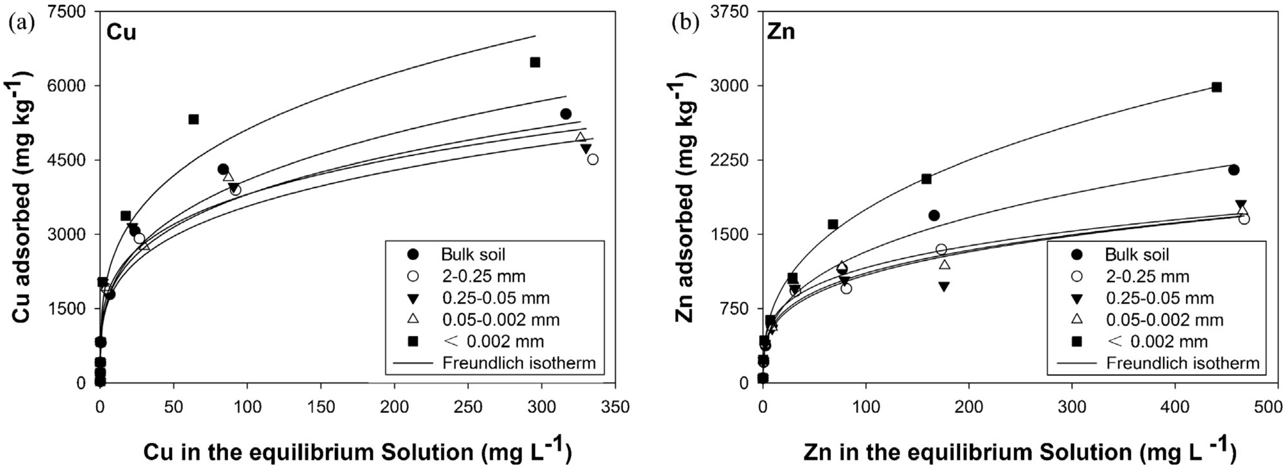

Fig. 2. Adsorption isotherms of Cu (a) and Zn (b) onto bulk soil and aggregates, the experimental data are reported as points and Freundlich model by curves.

Table 3
Langmuir and Freundlich model parameters and *R*-squared values calculated from isotherm experimental data of Cu and Zn.

Particle size mm	Langmuir			Freundlich		
	K_L (l/mg)	q_m (mg/kg)	R^2	K_F (l/kg)	n^{-1}	R^2
Cu adsorption						
Bulk soil	0.0624	5441.39	0.9720	1029.83	0.2998	0.9663
2–0.25	0.1595	4224.26	0.9500	1037.23	0.2682	0.9229
0.25–0.05	0.4570	4169.84	0.9512	1204.90	0.2500	0.9101
0.05–0.002	0.1218	4553.44	0.9203	1069.27	0.2757	0.9557
<0.002	0.1115	6230.10	0.9408	1349.59	0.2895	0.9359
Zn adsorption						
Bulk soil	0.0221	2211.69	0.9284	283.78	0.3347	0.9920
2–0.25	0.0629	1475.36	0.8808	316.56	0.2723	0.9799
0.25–0.05	0.0641	1438.06	0.7895	297.41	0.2819	0.9285
0.05–0.002	0.0775	1494.85	0.8842	366.73	0.2508	0.9609
<0.002	0.0160	3205.27	0.9409	334.10	0.3600	0.9974

Table 4
Fitted simple linear regressions of q_m to SOC, CEC, free iron oxide content in the form of $y = a + bx$.

y	X	a	b	R^2	P value
q_m (Cu)	SOC	−0.206	0.127	0.7401	0.0389
	CEC	−1.618	0.152	0.4820	0.1180
	Free Fe_2O_3	3.389	0.102	0.5971	0.0790
q_m (Zn)	SOC	−4.96	0.115	0.8730	0.0129
	CEC	−4.346	0.146	0.6960	0.0499
	Free Fe_2O_3	0.522	0.0962	0.7783	0.0305

with respect to CEC and free iron oxide. This is in keeping with the result of Yin et al. [16,39] who likewise believed that SOM had a large sorption capacity toward metals among the various reactive soil constituents.

3.3. Effect of the pH on the adsorption and desorption

The pH is considered as the most important factor that influences the adsorption of heavy metals in soil. From the pH-adsorption amount curves (Fig. 3(a) and (b)), it can be seen that the adsorption amount was strongly pH dependent. The reason for this trend, as discussed in many other similar research [40], can be explained as follow: when the pH value is low, metal cation faced competition with abundance of H^+ for available permanent charged sites, so the adsorption of heavy metal cation onto soil is limited; while at high pH value, this competition becomes weak, and thus, more metal is adsorbed. Therefore, under low pH condition, it is favorable for the release of Cu and Zn from soil to solution and increasing their migration risk to surface water and groundwater through runoff and leaching. Compared with Zn, Cu is more affected by pH change and this may attribute to different hydrolysis ability of these two metals [41]. The adsorption amount of the < 0.002 mm fraction is higher than the other size fraction in the pH scope of experiments, especially for Zn at relative high pH condition.

The parameter K_d indicates the ratio of metal between soil phase and solution, which is an important indicator for comparing the adsorption capacity of adsorbent. Based on the simple metal reaction equation: $S(OH)_n + M^{2+} \leftrightarrow (SO_n - M)^{(2-n)+} + nH^+$, researchers [42] proposed a formula for the relation between K_d and pH, Eq. (5):

$$lg(K_d) = lg(k) + x \times \text{pH} \tag{5}$$

where, x represent the number of releasing H^+ when a M^{2+} ion is adsorbed; pH is the balanced pH value of solution. Our analysis showed that there were remarkable relations between K_d and pH in the adsorption reaction of Cu and Zn (Cu: $0.9825 \le R^2 \le 0.9982$, $P = 0.0023$; Zn: $0.9838 \le R^2 \le 0.9992$, $P = 0.0054$) (Table 5). The x values of Cu are much higher than Zn, suggesting that the amount of Cu adsorbed through specific adsorption is much more than Zn, and the result also explain the stronger ability of soil in adsorbing Cu. For different particle size aggregates, x_{Cu}:(<0.002 mm) > 0.25–0.05 mm > 0.05–0.002 mm > bulk soil > 2–0.25 mm; x_{Zn}: (<0.002 mm) > 005–0.002 mm > 0.25–0.05 mm > bulk soil > 2–0.25 mm. Some researchers [8] believed that activity of organic matter and types of minerals play significant role in metal enrichment and contribute to relative higher portion of specific adsorption in the fine fractions.

Under the condition of desorption experiments by using 0.01 M $NaNO_3$, the desorption of desorbed metal from the total adsorbed

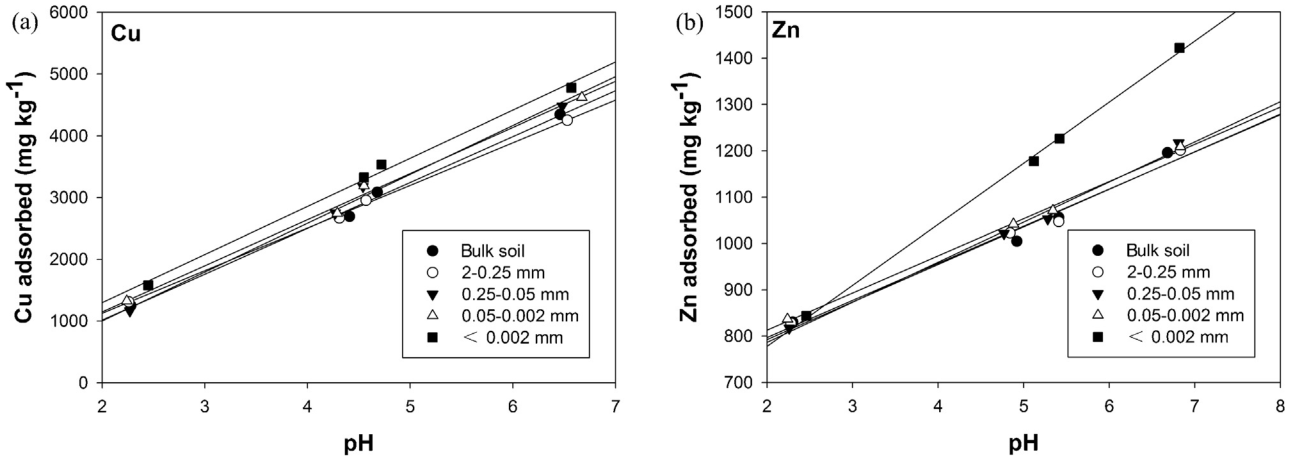

Fig. 3. Adsorption amounts of Cu (a) and Zn (b) under different balanced pH values.

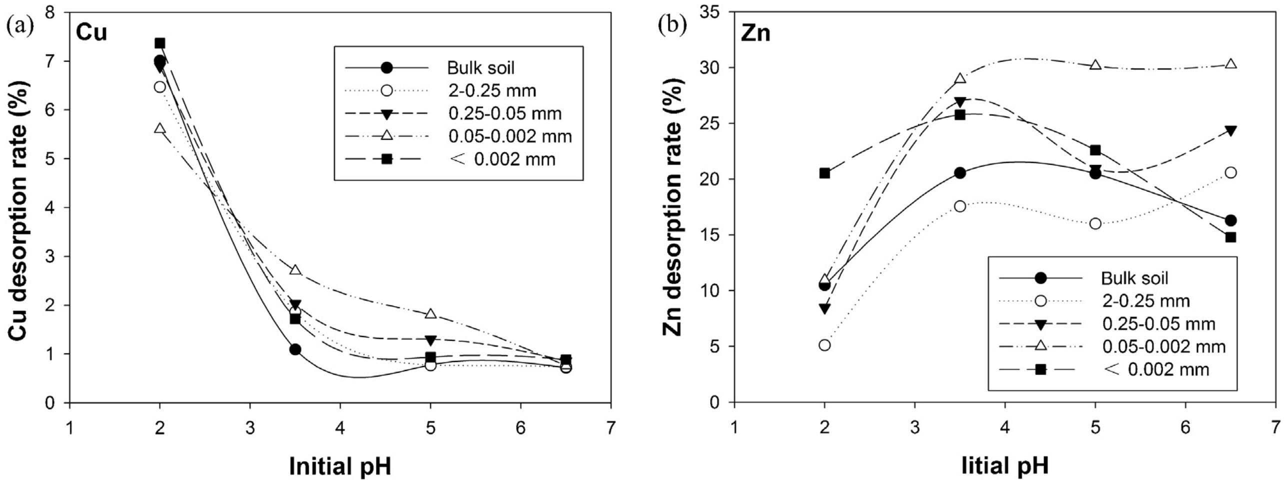

Fig. 4. Desorption rate of Cu (a) and Zn (b) under different initial pH values.

Table 5
Parameters calculated from the adsorption data at different balanced pH values by using the formula: $lg(K_d) = lg(k) + x \times \text{pH}$.

Particle size (mm)	Cu adsorption				Zn adsorption			
	lg (k)	x	R^2	P value	lg (k)	x	R^2	P value
Bulk soil	−0.0598	0.3875	0.9982	0.0006	0.8907	0.0445	0.9838	0.0054
2–0.25	0.1055	0.3493	0.9981	0.0006	0.8947	0.0438	0.9908	0.0031
0.25–0.05	−0.2152	0.4340	0.9930	0.0023	0.8816	0.0473	0.9970	0.0010
0.05–0.002	−0.0549	0.4107	0.9952	0.0016	0.8897	0.0478	0.9855	0.0048
<0.002	−0.0925	0.4521	0.9825	0.0006	0.8426	0.0673	0.9992	0.0003

of Cu decreased as the initial pH drop (Fig. 4(a)). The desorption rate (%) was very low when the pH exceed 3.5, and there was no obvious desorption phenomena existed for all the fractions at the initial pH of 6.5. Increasing of pH result in more OH^- binding Cu^{2+}, therefore the desorption of Cu^{2+} become more difficult [20,43]. Opposite to the situation of Cu, with the increasing of initial pH, the desorption of Zn increased in general (bulk soil and the < 0.002 mm fraction show downward trend when the pH > 3.5) (Fig. 4(b)). On one hand, such difference may be due to higher hydrolysis constant of Zn^{2+} relative to Cu^{2+} in solution [44], the influence of hydroxylation is little within this range of pH. On the other hand, there is more nonspecific adsorption (electrostatic adsorption) for Zn, surface negative charge will increase with the increase of pH and therefore result in more adsorption and desorption of Zn ions. However, at higher pH value, the effect of electrostatic adsorption becomes weak for the increase of OH^-, more stable metal hydroxyl compounds will be formed by hydroxylation and lead to less desorption amount [45,46]. pH has a greater effect on the desorption of Zn than Cu for the desorption of Zn^{2+} (approximately 5–30%) is higher than that of Cu^{2+} (approximately 0–8%), and this further illustrate more specific adsorption process happens during the adsorption process of Cu which consistent with the conclusion of previous adsorption experiments.

For different particle size aggregates, in the lower pH range (pH < 3), desorption of the <0.002 mm fraction was the highest, especially for Zn (actually, due to larger adsorption amount, the desorption amount of this fraction is the highest). Specific adsorption combined with organic matter, Fe_2O_3 etc. will be affected by amount of H^+ at low pH value, therefore the desorption amount of clay-size fraction aggregate relative higher.

3.4. Incubation experiment

3.4.1. Heavy metal content in various soil particles

The aim of incubation experiments was to understand the accumulation and speciation distribution characteristics of heavy metals in different size fractions of soil aggregates under the conditions close to nature. After 60 days of pollution incubation, almost all of soluble Cu (100%) and Zn (approximately 92%) transferred to integrate speciation bond to different soil constituents (Fig. 5). It is found that metals were tended to enrich in the finest fraction aggregate (<0.002 mm).

Accumulation factor AF_x [8] was used to estimate the distribution characteristic of metals in different particle-size aggregates, Eq. (6):

$$AF_x = \frac{X_{fraction}}{X_{bulk}} \quad (6)$$

where, $X_{fraction}$ and X_{bulk} are concentrations of metal (mg/kg) in a given particle size fraction and bulk sample, respectively. The AF_x

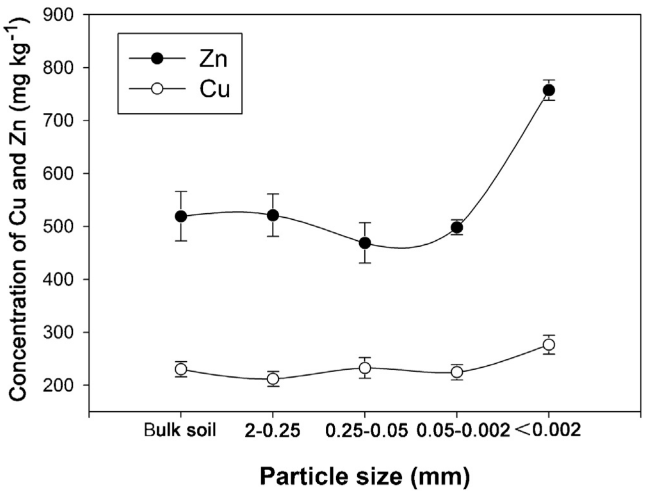

Fig. 5. Cu and Zn content in the bulk soil and various size fractions of aggregates after 60 days of incubation.

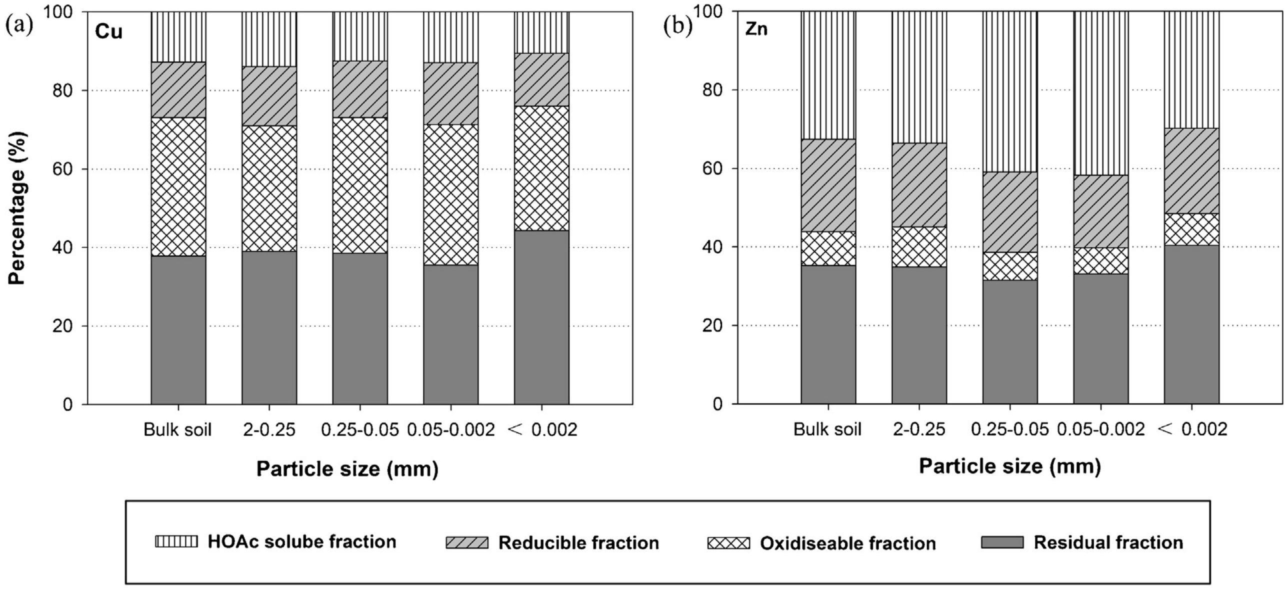

Fig. 6. Formation distribution of Cu (a) and Zn (b) in bulk soil and various size fractions of aggregates, result of the metal fractionation were obtained with the BCR method as introduced in the paper [28].

Table 6
Contributions of each fraction to the overall adsorption.

Particle size (mm)	Adsorbed mass contributed to the overall adsorption (mg/kg)	
	Cu	Zn
Bulk soil	205.44	456.13
2–0.25	18.37	45.13
0.25–0.05	49.29	98.59
0.05–0.002	99.79	212.71
<0.002	41.44	109.24

of Cu and Zn in the clay-size aggregates, with the values of 1.20 and 1.46, respectively, are greater than that of other particle size and are in good agreement with the result of adsorption isotherms experiments. Ajmone-Marsan et al. [47] found on average 33–37% of Cu and Zn accumulated in the <2 μm fraction of soil particles in five European cities and the AF_x values of the two metals were significantly higher than other fractions. It seems that, for red paddy soil, similar situation also exists. The contribution of each fraction to the overall adsorption of Cu and Zn onto bulk soil (Table 6) can be calculated by the product of $X_{fraction}$ and the mass percentage of the fraction in bulk soil. For both Cu and Zn, the contribution of the 0.05–0.002 fraction is the largest, which is mainly due to its highest mass percentage. It also observed that the adsorbed mass contributed to the overall adsorption of the <0.002 mm fraction (19.84% and 23.46% for Cu and Zn, respectively) was higher than its mass percentage (16.80%) in bulk soil. Therefore more attention should be paid to the finer particles when making health risks assessment and carrying out soil remediation for their in environment.

3.4.2. *Heavy metal distribution in different soil particles*

From the results of fraction analysis of bulks soil and aggregates by using BCR method, most of foreign Cu (71–76%) transferred to more stable fractions (Oxidiseable fraction and Residual fraction) (Fig. 6(a)), while a considerable part of Zn (29.9–41.7%) in the soil was acid soluble fraction (Fig. 6(b)). Thus it can be seem that Zn shows a higher activity than Cu in the soil environment. Though not very significant difference was detected among formation distribution of various aggregates, the <0.002 mm fraction was still observed to have the lowest acid soluble fraction and highest residual fraction comparatively. Quenea et al. [16] also found metals associated with the coarse fractions of the soil were mainly under relatively labile forms, although they extracted bio-available metals by using EDTA. Moreover, some studies have shown that the speciation, solubility and mobility of metals could be influenced by functional groups of different activity in organic matter [48]. Dabkowska-Naskret [49] held the view that the organic matter of the clay fraction could have a stabilization effect on the metals and reduce their bioavailability due to its higher stability against microorganism degradation. However, the speciation distribution of heavy metals in soils was determined by the intergraded effect of the soil constituents including organic matter and the environmental factors such as pH, temperature and moisture condition, etc. [50,51]. Furthermore, it will be more complicate with the aggregates as the study object, which put forward to a requirement for further research. From the result obtained, soil texture showed some effect on the speciation of metal retained in soil and the fine soil particle seemed to be the final carrier of metals in the soil.

4. Conclusion

Batch adsorption and incubation experiments were applied to study the adsorption characteristics of Cu and Zn onto different aggregates from red paddy soil. In the kinetic adsorption experiments, the adsorption data were successfully fitted by the pseudo-second order model for both Cu and Zn, the initial adsorption rate (ν_0) increased with the decrease of particle size except for the 0.05–0.002 mm fraction. Freundlich equation was more accurate than Langmuir equation to fit the adsorption characteristics under different initial metal concentration in the isotherms adsorption experiments for the two metals. More organic matter, CEC and free iron oxide contents accounted for the maximum q_m value of the clay-size fraction. The adsorption amount of Cu and Zn increased apparently as the pH increase. More specific adsorption in the aggregates of < 0.002 mm fraction lead to more desorption amount at low pH condition, so it will bring a greater pollution risk for this fraction when the external pH changed since their adsorption capacity is the highest as well. After being introduced into the soil, water-soluble Cu and Zn were more likely to enrich in the clay-size aggregates and the fine soil particle was seemed to be the final carrier of metals in the soil.

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