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Research Article

Sorption and Desorption of Copper and Cadmium in a Contaminated Soil Affected by Soil Amendments

Sorption and desorption processes control the bioavailability of heavy metals in the environment. Soil incubation and batch experiments were conducted to evaluate the effects of soil amendments on sorption, and desorption of Cu²⁺ and Cd²⁺ in a contaminated acidic paddy soil. The study showed that limestone and silicon fertilizer increased Cu²⁺ and Cd²⁺ sorption 2.43- and 1.13-fold, which was higher than calcium magnesium phosphate, Chinese milk vetch, pig manure, and peat. The Freundlich equation fitted sorption of Cu²⁺ and Cd²⁺ better than the Langmuir and Temkin equations. High desorption percentages of sorbed Cu^{2+} (mean of 67.1%) and Cd^{2+} (mean of 78.2%) were observed from the contaminated soil. Limestone and silicon fertilizer significantly decreased the desorption percentage of sorbed Cu^{2+} to 11.4 and 40.0%, respectively, and significantly decreased the desorption percentage of sorbed Cd^{2+} to 42.5 and 61.0%, respectively. However, the other four amendments did not show significant impact. Increasing soil pH significantly increased contents of sorbed Cu²⁺ and Cd²⁺, and negatively influenced desorption of sorbed Cu²⁺ and Cd²⁺. Application of amendments changed Cu and Cd fractions in soils, which might affect the sorption and desorption of Cu^{2+} and Cd^{2+} . The effects of soil amendments on sorption and desorption of heavy metals may be useful for predication of their remedy efficiency to heavy metal contamination.

Keywords: Bioavailability; Heavy metal fractions; Paddy soil; pH; Remedy efficiencies *Received:* July 23, 2015; *revised:* December 5, 2015; *accepted:* July 25, 2016 **DOI:** 10.1002/clen.201500555

1 Introduction

Heavy metals are introduced to agricultural soils by industrial and agricultural activities including mine exploration, metallurgy industry, irrigation of wastewater, and application of sewage sludge, fertilizers, and pesticides. More and more, heavy metals are accumulated in arable soils, resulting in degradation of soil quality and soil productivity [1]. Some of these metals enter the food chain and cause physiological, and health problems on humans [2]. Many technologies such as phytoremediation, electro-remediation, chemical remediation, and agro-ecological engineering have been used to mitigate heavy metal contamination in soils [3, 4]. Among those, chemical remediation has been widely used by adding nontoxic inorganic or organic amendments to soils to stabilize heavy metals [5–8].

In order to evaluate the degree of heavy metal contamination in soils, the total quantity of heavy metals in soil is usually used as one of the most important indicators. However, concentration of heavy metals in soil solution mostly determines the actual environmental exposure or risk. The transport of metals within soil or even to groundwater also depends on the metal concentration in a solution phase [9]. As the retention mechanism of heavy metal ions at soil surfaces is often unknown, the term "sorption" is preferred, which in general refers to the process involving the loss of metal ions from an aqueous to a contiguous solid phase. Several retention processes such as precipitation, co-precipitation, fixation, diffusion, and surface sorption may contribute simultaneously toward metal immobilization and/or adsorption [10, 11]. After heavy metals enter soil, they are subjected to the primarily and inevitable reaction processes such as sorption and desorption. It was suggested that sorption and desorption of heavy metals on soil surfaces are the key processes that control their concentrations in soil solution. They ultimately affect the transfer, transformation, bioavailability, and ecotoxicity of metals in soil-plant systems [11, 12]. Hence, the study on sorption and desorption characteristics of heavy metals in soil would have greater practical significance to understand, and control the environmental behaviors of metals in soil-plant systems.

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Abbreviations: AAS, atomic absorption spectrometer; CEC, cation exchange capacity; CMV, Chinese milk vetch; DOM, dissolved organic matter; Eh, oxidation reduction potential; L, limestone; PE, peat; PF, Ca-Mg-P fertilizer; PM, pig manure; Si, CaSiO₃; SOM, soil organic matter; TC, total C; TCd, total Cd; TCu, total Cu; TN, total N; TK, total K; TP, total P; TZn, total Zn.

Application of amendments in heavy metal contaminated soils could affect soil physical and chemical properties such as soil texture, specific surface area, cation exchange capacity (CEC), pH, oxidation reduction potential (Eh), and soil organic matter (SOM). It also could affect the transformation of heavy metals among various fractions [4, 7, 13]. Furthermore, the application of amendments might affect the sorption/desorption characteristics of heavy metals in soils as well as heavy metal fractions [14]. McBride [15] reported that the sorption behavior of Cu, Cd, Zn, and Ni in soils varied from soil to soil and was influenced by soil properties, such as pH, SOM, CEC, and clay contents. Thereby, during the remediation process of heavy metal contamination in soils, the amendments used may decrease the bioavailability of heavy metals and their uptake by plants through affecting their sorption/desorption characteristics in soils. More researches are needed to understand the real effects, and to predict their transport and fate in soils.

Variable charge soils are distributed widely in tropical and subtropical regions of China. These soils carry both positive and negative charges on their surfaces, and therefore, can adsorb both anions and cations [16]. Furthermore, because of their low pH and low effective CEC, heavy metals in the soils have higher bioavailability and ecotoxicity to plants, and human being. The soil amendments such as limestone, calcium magnesium phosphate, calcium silicate, Chinese milk vetch, pig manure, and peat can decrease the bioavailability of Cu and Cd in a contaminated paddy soil, and affect the distribution and accumulation of Cu and Cd in the soil-rice system [17, 18]. Bolan et al. [5, 6] reported that addition of phosphate and lime decreased the concentration of available Cd in seven variable charge soils, and then decreased Cd uptake by Indian mustard. Cui et al. [19] applied apatite, lime, and charcoal to a Cu and Cd contaminated variable charge soil, and found that those amendments significantly decreased CaCl₂extractable Cu and Cd in soil. A 3-year experiment conducted by Bian et al. [20] confirmed continuous decrease of CaCl2-extractable Cd in a contaminated paddy field with biochar amendment, which also significantly reduced Cd concentration in rice roots, shoots, and grains. However, previous works mostly focused on the change of available (extracted by CaCl₂ solution) heavy metals concentrations in soils with amendments application and the transport of heavy metals in soil-plant systems. Few studies have been conducted to investigate the sorption and desorption characteristics of heavy metal ions after application of amendments to soils. Actually, the sorption and desorption characteristics directly affect mobility of heavy metals in soils and their transport regulatory mechanisms in soil-plant systems. Therefore, a more detailed understanding of the

sorption and desorption behavior of heavy metals in the soils with addition of amendments is required.

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The aims of this study were to evaluate the influence of soil amendments on the sorption and desorption of copper and cadmium in a contaminated paddy soil, and to explore their mechanisms. The results will be useful for the studies on other soils with similar physicochemical characteristics in the world and could provide knowledge in order to deeply understand the bioavailability of heavy metals with the application of amendments to soils, and evaluate the remedy efficiencies of soil amendments.

2 Materials and methods

2.1 Soil and amendments description

Top 20 cm of a metal-contaminated soil sample was collected from a paddy field located in Sumen Village, Guixi City, Jiangxi Province, central subtropical China (28°20.307'N and 117°14.133'E). The paddy field in the study area had been irrigated by sewage from an adjacent smelting factory for more than 20 years [21]. The soil contained high concentrations of Cu and Cd, that significantly exceeded the environmental quality standard for agricultural soils (50 mg kg⁻¹ Cu and 0.3 mg kg⁻¹ Cd in GB 15618-1995) issued by the State Environmental Protection Administration of China. The paddy soil was developed from red sandstone with 13.0% clay, 40.5% silt, and 46.5% sand, and the main soil properties are shown in Tab. 1.

Among the soil amendments used for this study, limestone, Chinese milk vetch, and pig manure were from a local village; calcium magnesium phosphate (Ca–Mg–P fertilizer) was from Yingtan Yifeng Phosphate Fertilizers, China; silicon fertilizer (CaSiO₃) was from Sinopharm Chemical Reagents, China; peat was from Jiamushi Nongyou Peats, China. Table 1 shows some chemical properties and total heavy metal concentrations of the amendments.

2.2 Chemical analysis of solids

All tests were performed at constant dry weight. The pH of the soil, Ca–Mg–P fertilizer, pig manure, and peat was measured in water suspension, water/solid, 2.5:1 w/w, by a combined glass pH electrode. The pH of limestone, silicon fertilizer, and Chinese milk vetch was measured with the same pH electrode at water/solid ratios of 5:1, 5:1, and 10:1, respectively. Chinese milk vetch was digested with concentrated HNO₃ and H_2O_2 , while soil and other amendments were digested with concentrated HNO₃, HF, and HClO₄ [22]. The concentrations of total Cu (TCu), total Cd (TCd), total Zn (TZn) in the

Table 1. Selected chemical properties of soil and amendments (on dry weight basis)

			$ m gkg^{-1}$				${ m mgkg^{-1}}$		
	pH	SOM	TC	TN	TP	ТК	TCu	TCd	TZn
Soil	4.51	26.5	Nd	1.68	0.35	10.96	1073	6.79	71.1
Limestone	12.38	Nd	Nd	Nd	Nd	Nd	6.52	8.60	20.8
Ca-Mg-P fertilizer	7.36	Nd	Nd	Nd	Nd	Nd	1310	4.81	1076
Silicon fertilizer	10.85	Nd	Nd	Nd	Nd	Nd	0.57	7.58	5.11
Chinese milk vetch	6.11	Nd	441	28.2	Nd	Nd	16.4	0.42	Nd
Pig manure	7.65	Nd	185	21.2	Nd	Nd	725	4.11	1417
Peat	4.03	Nd	322	22.0	Nd	Nd	13.8	1.94	44.8

Nd, not detected.



digested solutions were determined by atomic absorption spectrometry (AAS; Hitachi 180, Japan). SOM was determined by potassium dichromate oxidation method. Total N (TN) was determined by the semimicro-Kjeldahl method after digesting the soil with HClO₄ and HF. Total P (TP) was determined by acidic molybdate-ascorbic acid blue spectrophotometric method and total K (TK) was determined by flame photometry. Total C (TC) and total N (TN) of Chinese milk vetch, pig manure, and peat were determined by the potassium dichromate oxidation-sulfuric acid method and the semimicro-Kjeldahl method, respectively [22].

2.3 Incubation experiment

Soil samples were air-dried and passed through a 1-mm sieve, and all amendments were passed through a 0.149-mm sieve prior to the incubation experiments. The experiment was performed in seven treatments and triplicate replicates per treatment (Tab. 2). Various amendments were homogeneously mixed with 100 g of air-dried contaminated soil at specific application rates on dry weight basis (Tab. 2). The water content of the soil was adjusted to 65% of water holding capacity by adding deionized water with an automatic pipette and was placed in a 500-mL plastic bottle. The bottles were then placed in an incubator at 25°C and 70% relative humidity. Throughout the incubation period, water losses exceeding 10% of the initial values were compensated by addition of deionized water. Soil samples were taken on day 120 after incubation, and soil pH was measured at water/solid ratio w/w of 2.5:1. The soil samples were airdried, passed through a 1-mm sieve, and then used for the sorption and desorption experiments.

2.4 Sorption and desorption experiments

2.4.1 Sorption stage

Sorption experiments were conducted in batch conditions on the soil and soil mixtures. Copper and Cd were added as Cu(NO₃)₂ and Cd(NO₃)₂ in 25.0 mL of 0.01 M NaNO₃ as background electrolyte (initial pH 5.5). The Cu^{2+} concentrations in the solution ranged from 0 to 140 mg L^{-1} with the increment of 20 mg L^{-1} , while the Cd²⁺ concentrations ranged from 0 to 35 mg L^{-1} with the increment of 5 mg L^{-1} . Soil (1 g) and the centrifuge tube were weighed together as W_1 (g), and the metal solution was added to the centrifuge tube. The centrifuge tubes were shaken at 25°C in a rotary shaker for 24 h. The slurry in the tube was centrifuged at 4000 rpm for 10 min. The supernatant was collected and filtered, and its concentrations of Cu and Cd were measured by AAS. The amount of sorbed Cu²⁺ or

Table 2. Experimental design for the treatments of the incubation experiment.

CK Only soil	asis)
L $4 g kg^{-1}$ limestonePF $4 g kg^{-1}$ Ca-Mg-P fertilizerSi $4 g kg^{-1}$ CaSiO3CMV $8 g kg^{-1}$ Chinese milk vetchPM $8 g kg^{-1}$ pig manurePE $24 g kg^{-1}$ peat	

Cd²⁺ was calculated as the difference between the amount added initially and the remaining amount in solution after equilibration, as described in Eq. (1). All measurements were run in triplicate.

$$S = (C_0 - C)\frac{V}{m} \tag{1}$$

where S is the amount of sorbed Cu^{2+} or Cd^{2+} (mg kg⁻¹), C_0 is the concentration of Cu^{2+} or Cd^{2+} in the initial solution (mg L⁻¹), C is the concentration of Cu²⁺ or Cd²⁺ remaining in the solution after equilibration (mg L^{-1}), V is the volume of the equilibrium solution (mL), and *m* is the dry weight of soil (g).

2.4.2 Desorption stage

Immediately after sorption, desorption experiments were carried out. The centrifuged residues and centrifuge tube were weighed together as W_2 (g). The residues were resuspended in 25 mL of 0.1 M NaNO3 and shaken on the rotary shaker for 2 h at 25°C for equilibration, and the mixture was centrifuged at 4000 rpm for 10 min after equilibration. The supernatant was collected and filtered, and the concentrations of Cu²⁺ and Cd²⁺ were measured by AAS. The quantity of Cu²⁺ or Cd²⁺ desorbed from soil was calculated by the difference between the amount in solution after equilibration and the remaining amount in the centrifuged residue solution in sorption stage, as described in Eq. (2).

$$S = C_{\rm des} \times (25 + W_2 - W_1) - C_{\rm sor} \times (W_2 - W_1)$$
(2)

where S is amount of desorbed Cu^{2+} or Cd^{2+} (mg kg⁻¹), C_{des} is the concentration of Cu^{2+} or Cd^{2+} in the equilibration solution (mg L^{-1}), $C_{\rm sor}$ is the concentration of ${\rm Cu}^{2+}$ or ${\rm Cd}^{2+}$ remaining in the centrifuged residue solution in the sorption stage (mg L^{-1}), W_1 is the weight of dry soil and centrifuge tube (g), and W₂ is the weight of centrifuged residues and centrifuge tube (g).

2.5 Statistical analysis

Langmuir, Freundlich, and Temkin equations were employed to model the sorption data using the non-linear least square analysis [23]. The Langmuir equation can be presented as:

$$X = \frac{KCX_m}{1 + KC}$$
(3)

where X is the amount of sorbed metal ions $(mg kg^{-1})$, X_m is the maximum sorption capacity (mg kg $^{-1}$), C is the concentration of the metal ions in the equilibrium solution (mgL^{-1}) , and K is a constant related to the energy of sorption.

The Freundlich equation is as follows:

$$X = K C^{\frac{1}{n}}$$
⁽⁴⁾

where X is the amount of sorbed metal ions $(mgkg^{-1})$, C is the concentration of the metal ions in the equilibrium solution $(mg L^{-1})$, and K and n are constants.

The Temkin equation is as follows:

$$X = K_1 \ln(K_2 C) \tag{5}$$

where X is the amount of sorbed metal ions $(mg kg^{-1})$, C is the Cu^{2+} sorption concentration of the metal ions in the equilibrium solution $(mg L^{-1})$, Ca-Mg-P fertiliz

and K_1 and K_2 are constants. The regression was evaluated using SPSS 13.0 statistics software at significance levels of p < 0.05 (significant) and p < 0.01 (extremely significant).

3 Results

3.1 Sorption isotherms of Cu^{2+} and Cd^{2+}

Copper and Cd sorption isotherms on soils with different amendments are shown in Fig. 1. When the equilibrium metal concentrations were low, the amounts of Cu^{2+} and Cd^{2+} sorbed to soils increased sharply with equilibrated metal concentrations. As Cu^{2+} and Cd^{2+} concentrations increased in the equilibrium solution, the slope of the sorption isotherm leveled off, indicating that the sorbent reached its maximum capacity. The amount of sorbed Cu^{2+} was much higher compared to Cd^{2+} . A similar result was also reported by Covelo et al. [24].

To describe the sorption characteristics of Cu^{2+} and Cd^{2+} onto soil, experimental data obtained from the sorption experiment were evaluated with Langmuir, Freundlich, and Temkin models. As Özkan et al. [25] noted that the analysis of isotherm data is important to develop an equation that accurately represents the results and could be used for design purposes. The calculated parameters for the three models are presented in Tabs. 3 and 4. The results showed that the data fitted the three equations well with correlation coefficients (r) > 0.93. The Freundlich equation was reported to be more suitable to the Langmuir equation for sorption of cations or anions by soil [26, 27]. By comparing the *r*-values (Tabs. 3 and 4), the Freundlich equation represents a better fit to the experimental data than the Langmuir and Temkin equations in sorption of Cu^{2+} and Cd^{2+} in this study.

Application of amendments induced an increase in Cu²⁺ and Cd²⁺ sorption onto soil (Fig. 1), and the increasing effects varied with the types of amendments. Limestone and silicon fertilizer had a greater impact on the sorption than the other amendments. Compared with the control, limestone and silicon fertilizer significantly increased

Cu²⁺ sorption 1.73–3.19-fold and 0.66–1.99-fold, respectively. Ca–Mg–P fertilizer, Chinese milk vetch, pig manure, and peat also increased Cu²⁺ sorption by 7.5–30.6%, 4.6–41.3%, 1.2–6.4%, and 2.8–22.0%, respectively. However, the differences were not statistically significant, as compared with the control. In general, the increase of Cu²⁺ sorption induced by amendments was more substantial than that of Cd²⁺; limestone and silicon fertilizer

enhanced Cd^{2+} sorption by 77.4 and 29.1%, whereas, Cu^{2+} sorption was increased by 243 and 113%. The effects of different amendments on sorption of Cu^{2+} and Cd^{2+} followed the order: limestone > silicon fertilizer > Ca-Mg-P fertilizer > Chinese milk vetch > peat > pig manure.

3.2 Desorption isotherms of Cu²⁺ and Cd²⁺

Figure 2 shows the desorption isotherms of Cu^{2+} and Cd^{2+} sorbed by the soils in different treatments. The amounts of Cu^{2+} and Cd^{2+} desorbed increased with the sorbed amounts of Cu^{2+} and Cd^{2+} by soils. In order to describe the relationship between sorption and desorption of Cu^{2+} and Cd^{2+} in the soils, the data obtained from the desorption experiment were evaluated with several models. The exponential equation ($Y = e^x$) fitted the data the best, while all correlative coefficients (r) were >0.95 (Tab. 5).

Application of all six amendments reduced desorption of sorbed Cu^{2+} and Cd^{2+} , and limestone and silicon fertilizer had higher reduction effects than the other amendments (Fig. 3). In the control treatment, the desorption percentage of sorbed Cu^{2+} ranged from 55.9 to 72.3%, while the desorption percentage of sorbed Cd^{2+} was between 75.4 and 80.2%. After soils were incubated with limestone and silicon fertilizer for 120 days, only 2.2–18.3% and 37.1–43.3% of sorbed Cu^{2+} and 15.6–52.9% and 54.2–64.6% of sorbed Cd^{2+} were desorbed from the amended soils, and the mean desorption percentage of sorbed Cu^{2+} and Cd^{2+} was significantly decreased. However, the other four amendments had no significant influence on the desorption percentage of Cu^{2+} followed the order: Control > Ca–Mg–P fertilizer > peat > pig manure > Chinese milk vetch > silicon fertilizer > limestone, and desorption percentage of Cd^{2+} followed the order: Control > peat > peat



Figure 1. Sorption isotherms of Cu^{2+} and Cd^{2+} on soils in different treatments.



		Langmuir			Freundlich			Temkin		
Treatment	Xm	Κ	r	K	n	r	<i>K</i> ₁	<i>K</i> ₂	r	
СК	2500	0.0032	0.963**	10.52	1.123	0.998**	288.2	0.081	0.984**	
L	2000	0.2083	0.996**	603.8	3.601	0.993**	288.3	7.832	0.996**	
PF	1428	0.0091	0.969**	22.58	1.321	0.987**	288.3	0.112	0.994**	
Si	1428	0.0409	0.995**	161.5	2.396	0.997**	288.7	0.467	0.993**	
CMV	1250	0.0109	0.992**	27.57	1.427	0.994**	262.5	0.121	0.991**	
PM	2500	0.0034	0.938**	11.74	1.147	0.996**	284.3	0.085	0.985**	
PE	1667	0.0065	0.947**	16.63	1.232	0.988**	281.5	0.099	0.996**	

Table 3. Parameters of sorption isotherm models for Cu^{2+} in different treatments

**Significance level at p < 0.01.

Ca-Mg-P fertilizer > pig manure > Chinese milk vetch > silicon fertilizer > limestone, the only difference in order between these two elements was Ca-Mg-P fertilizer and peat.

4 Discussion

4.1 Effects of amendments on sorption of \mbox{Cu}^{2+} and \mbox{Cd}^{2+}

Because of the inhomogeneity of soil surface, there are high and low affinity sorption sites in soils. The high affinity sorption site has high bonding energy and heavy metal ions are sorbed through specific sorption mechanisms such as co-precipitation between heavy metal ions and Fe-Mn oxides surface or soil particle surface precipitation of chelates formed by soil particles and heavy metal ions [28]. The low affinity sorption site has rather low bonding energy and heavy metal ions are sorbed through the nonspecific sorption mechanism of electrostatic attraction [29]. When concentrations of heavy metal ions are low, the high affinity sorption site is the preferred site for ions, whereas, at high concentrations, the low affinity sorption site is also occupied by metal ions [28]. In this study, the increase of sorbed Cu^{2+} and Cd^{2+} with the increasing concentrations of Cu^{2+} and Cd^{2+} in the equilibrium solution (Fig. 1) might be attributed to the change of sorption sites. Furthermore, the amount of sorbed Cu^{2+} was much higher compared to Cd^{2+} , which might be attributed to its lower hydrolysis constant of first step (pK1), solubility product of hydroxide precipitate and carbonate precipitate than Cd^{2+} [30].

In the Freundlich model, *K* indicates the adsorbing capacity of soil, and *n* is considered as a measurement of the intensity of sorption force between soil and heavy metal ions. If n < 0.5, the sorbate is usually difficult to be sorbed on soil [31]. In this study, n-values were all > 0.5 for Cu²⁺ and Cd²⁺ in the seven treatments, and the *n*-values of limestone and silicon fertilizer treatments were much higher compared to the control (Tabs. 3 and 4), indicating that these two amendments could significantly enhance the sorption of Cu²⁺ and Cd²⁺ on soil. Soil pH directly and indirectly influences all chemical processes, and consequently the behavior of trace elements in soils [32]. It is an important factor in affecting sorption and desorption of heavy metals by soil [33]. Shaheen [34] reported that the total amounts of Pb and Cd sorbed within the concentration range used in the sorption experiments were larger in alkaline than in acidic soils from Egypt and Greece. The increase of Cu²⁺ and Cd²⁺ sorption in this study might be attributed to the increase of soil pH caused by the amendments. After incubated with the amendments for 120 days, the soil pH was increased by 0.13-2.35 units (4.81-7.03 for amendment treatments and 4.68 for the control), except for peat [35]. For both Cu and Cd, K and n had a significant positive correlation with soil pH (p < 0.01). As a result, significant positive correlations were also found between soil pH and sorbed Cu²⁺ and Cd^{2+} (Tab. 6). Other researchers also reported that the sorption of Pb, Zn, and Cd by variable charge soils was pH dependent [19, 36]. An increase in soil pH causes deprotonatin of hydroxyl groups on the surface of iron and aluminum oxides, and thereby, results in the increase of variable negative charges on soil colloid surfaces. More variable negative charges could attract more Cu²⁺ and Cd²⁺ toward soil surfaces through electrostatic attraction [37, 38], thereby, enhancing heavy metal ions sorption by soil clay minerals or iron and aluminum oxides. On the other hand, increasing soil pH accelerated the transformation of Cu^{2+} and Cd^{2+} from M^{2+} to MOH^+ and M(OH)₂ through hydrolysis, decreased the energy obstacle of the two ions to bind to soil oxides surface, and then increased the

Table 4. Parameters of sorption isotherm models for Cd²⁺ in different treatments

	Langmuir			Freundlich			Temkin		
Treatment	Xm	Κ	r	K	n	r	<i>K</i> ₁	<i>K</i> ₂	r
СК	200.0	0.0814	0.982**	26.90	1.995	0.995**	43.87	0.810	0.981**
L	232.6	0.3981	0.994**	106.3	4.604	0.997**	33.35	21.60	0.985**
PF	232.6	0.0788	0.986**	29.28	1.923	0.998**	50.74	0.789	0.984**
Si	250.0	0.0973	0.979**	39.32	2.216	0.998**	53.27	1.032	0.976**
CMV	227.3	0.0748	0.984**	27.10	1.888	0.996**	49.35	0.750	0.983**
PM	217.4	0.0727	0.983**	25.73	1.892	0.998**	47.29	0.731	0.981**
PE	212.8	0.0802	0.986**	27.36	1.932	0.997**	47.34	0.781	0.985**

**Significance level at p < 0.01.

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600 140 CK 120 500 PF Si Desorbed Cu²⁺ (mg kg⁻¹) Desorbed Cd²⁺ (mg kg⁻ 100 CMV 400 PM PE 80 300 60 200 40 100 20 0 0 400 800 1200 1600 80 Ò 2000 0 40 120 160 200 240 Sorbed Cu²⁺ (mg kg⁻¹) Sorbed Cd²⁺ (mg kg⁻¹)

Figure 2. Desorption isotherms of Cu^{2+} and Cd^{2+} sorbed by soils in different treatments.

specific sorption by soil colloid surface [39]. Furthermore, increasing soil pH also allowed Cu^{2+} and Cd^{2+} to form stable complexes with SOM and manganese oxides, and then increased their sorption by soil. Ma et al. [40] reported that with increasing pH, more -COOHand -OH in soil colloids dissociated to form $-COO^-$ and $-O^-$, which can increase the ability of SOM to complex with Cu^{2+} , and thus, increase the sorption of Cu^{2+} .

SOM is an important part of soil composition, and it plays a key role in the physical, biological, and chemical processes in soil, including the sorption of heavy metal. In this study, the increases of SOM content caused by Chinese milk vetch, pig manure, and peat were also contributed to the enhancement of heavy metal sorption. Harter [33] stated that SOM is an important factor in affecting sorption of heavy metal ions by soil. Removal of organic matter in soil dramatically decreased the sorption of heavy metal ions [41]. Yu [42] reported that the contribution of organic matter to the total negative surface charges of the paddy soils (derived from red soils) was 5-42% with an average of 21%. In this study, after soil was incubated for 120 days, the quantity of SOM was increased along with minor decomposition of these organic materials, and therefore, the sorption of Cu^{2+} and Cd^{2+} was enhanced. Roth et al. [43] studied the effect of organic matter on adsorption of Cd on different granulometric soil fractions and found that increasing organic matter enhanced Cd²⁺ sorption by making the surface more negative. The decomposed products of organic amendments might also play an important role in the enhancement of Cu²⁺ and Cd²⁺ sorption. Dissolved organic matter (DOM) produced by the decomposition of organic amendments during the incubation period may form complex bridges between soil and heavy metal ions to increase the sorption of heavy metal ions by soil [44]. Organic matter has a strong affinity for Cu, especially at low concentrations [45]. The formation of inner-sphere complexes between organic matter and Cu2+ also referred to as chemisorption or specific sorption. Li et al. [46] also reported that DOM extracted from pig manure enhanced Cd sorption significantly. Moreover, organic matter adsorbed by soil oxides can further complex with Cu²⁺ and Cd²⁺ to form tri-complexes, and thus, increase Cu²⁺ and Cd²⁺ sorption [38]. In this study, the increase of Cu²⁺ and Cd²⁺ sorption in peat treatment might be attributed to the complexation effect

between Cu²⁺ or Cd²⁺ and the dissolvable or insoluble decomposed products of peat, as soil pH decreased slightly after the application of peat.

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After 120 days incubation, application of the six amendments significantly decreased the concentrations of water soluble and exchangeable Cu and Cd in soils but increased the concentrations of carbonate-bound, Fe-Mn oxides-bound, organic-bound, residual Cu and Cd by different levels [35]. Water soluble heavy metals exist in soil solution, and exchangeable heavy metals are immobilized on the surface of soils or sediments through nonspecific sorption mechanisms such as diffusion and complexation [47]. They are all available fractions and easy to be taken up by plants. Those available Cu or Cd in soils might occupy some sorption sites, and then, affect the sorption of Cu^{2+} or Cd^{2+} in the sorption solution to the soils. There are significant negative correlations between water soluble, exchangeable Cu or Cd in soils, and the amount of sorbed Cu²⁺ or Cd^{2+} (p < 0.01). Helios-Rybicka and Wójcik [48] studied sorption and desorption of several heavy metal by three mining wastes, and found that Cd sorption was increased consistently with the decrease of exchangeable Cd. Fe-Mn oxides in soils are effective sorbents and can significantly contribute to the sorption of trace metal ions [49]. Diagboya et al. [50] noted that iron oxides in soils enhanced

Table 5. Desorption isotherm equations for sorbed \mbox{Cu}^{2+} and \mbox{Cd}^{2+} in different treatments

	Cu		Cd		
Treatment	Equation	r	Equation	r	
CK L PF Si CMV PM PE	$\begin{split} Y &= 58.057 e^{0.0034 X} \\ Y &= 4.322 e^{0.0025 X} \\ Y &= 57.386 e^{0.0032 X} \\ Y &= 80.329 e^{0.0034 X} \\ Y &= 56.130 e^{0.0032 X} \\ Y &= 51.073 e^{0.0035 X} \\ Y &= 53.248 e^{0.0034 X} \end{split}$	0.966 0.984 0.988 0.990 0.992 0.983 0.988	$\begin{array}{l} Y = 22.745 e^{0.0117 X} \\ Y = 3.871 e^{0.0164 X} \\ Y = 24.158 e^{0.0103 X} \\ Y = 21.582 e^{0.0095 X} \\ Y = 19.933 e^{0.0119 X} \\ Y = 19.693 e^{0.0123 X} \\ Y = 21.323 e^{0.0117 X} \end{array}$	0.987 0.956 0.985 0.971 0.974 0.981 0.987	

Y is desorbed Cu^{2+} or Cd^{2+} (mg kg⁻¹), X is sorbed Cu^{2+} or Cd^{2+} (mg kg⁻¹).



Figure 3. Desorption percentage of Cu²⁺ and Cd²⁺ sorbed by soils in different treatments.

retention and retarded desorption of heavy metals with time. In this study, significant positive correlations were also found between carbonate-bound, Fe–Mn oxides-bound Cu or Cd and the amount of sorbed Cu²⁺ or Cd²⁺ (p < 0.01), indicating that the more of these two metal fractions, the less of exchangeable metals in soil. This resulted in more low affinity sorption sites, which would sorb more metal ions through the nonspecific sorption mechanism. This study indicated that soil amendments could affect heavy metal ions sorption by soil through changing the soil pH, SOM, and heavy metal fractions in soil.

4.2 Effects of amendments on desorption of sorbed Cu^{2+} and Cd^{2+}

Amendments increased sorption of heavy metals by soils and then alleviated heavy metal contamination in soils. However, when selecting suitable amendments for the remediation of heavy metal contamination in soils, the effects of amendments on desorption of heavy metals and their stabilities also should be considered because the stabilities were connected with the metal activity in soil. The sorption and desorption of heavy metal ions often co-exist in soils, and the factors that affect metal sorption also have fundamental impacts on desorption of sorbed metal ions. Figure 2 indicates that the amount of desorbed Cu^{2+} and Cd^{2+} from sorbed soils increased gradually with amounts of sorbed Cu^{2+} and Cd^{2+} , and this was probably due to heterogeneous diffusion [51] and the increase of nonspecific sorption. The metal ions sorbed through nonspecific sorption (electrostatic attraction) can be readily desorbed by neutral salt solution, whereas, those metal ions sorbed by specific sorption are in nonexchangeable fractions and only can be desorbed in acidic condition [52]. In this study, the high amounts of desorbed Cu^{2+} and Cd^{2+} might be attributed to the use of 0.1 M NaNO₃ as the desorption agent which can extract most of heavy metal ions fixed by electrostatic sorption.

Significant negative correlations were found between soil pH and desorption percentage of sorbed Cu^{2+} and Cd^{2+} (Tab. 6), which was similar to the results of Rashti et al. [53] who studied cadmium desorption behavior in ten sub-tropical soils and found that the rate of Cd desorption increased with a decrease in pH. The application of amendments increased soil pH and enhanced the concentration of OH– in soil solution, and then enhanced quantity of hydroxide precipitates. Therefore, the desorption potential of sorbed Cu^{2+} and Cd^{2+} was reduced. Wang et al. [54] found that the desorption capacities of Cd significantly decreased in leached cinnamon soil, brown earth, and castanozem soil with calcium carbonate addition, and the decrease of Cd desorption were attributed to the increase of soil pH. Arias et al. [55] also reported that desorption percentage of adsorbed Cu and Zn in the

Table 6. Coefficients of correlations among soil pH, sorbed Cu^{2+} or Cd^{2+} , and desorption percentages of sorbed Cu^{2+} and Cd^{2+}

Cu			Cd				
Added concentration (mg L ⁻¹)	$r_{\rm sor-pH}$	r _{des-pH}	Added concentration (mg L ⁻¹)	$r_{\rm sor-pH}$	$r_{\rm des-pH}$		
20	0.925**	-0.983**	5	0.985**	-0.980**		
40	0.956**	-0.975**	10	0.981**	-0.967**		
60	0.964**	-0.952**	15	0.969**	-0.955**		
80	0.970**	-0.948**	20	0.979**	-0.943**		
100	0.971**	-0.951**	25	0.967**	-0.958^{**}		
120	0.974**	-0.942**	30	0.955**	-0.930**		
140	0.977**	-0.947**	35	0.913**	-0.917**		

**Significance level at p < 0.01.

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surface layer of 27 acid soils in Spain decreased with the increase of soil pH.

Because of different mechanisms in sorption and desorption of heavy metal ions, not all sorbed Cu^{2+} and Cd^{2+} could be released from the soils in the desorption process. Filius et al. [56] found that irreversible-bound Cd occupied some special sorption sites on soil increased with increasing soil pH. Desorption of irreversible-bound Cd normally needs higher activation energy [38]. Morton et al. [57] also reported that Cu sorption irreversibility on montmorillonite was due to the formation of kinetically irreversible Cu dimer complexes or coordination of Cu on the high-energy sites of clay. At low pH, Cu^{2+} sorbed by soil surface usually exists as an extractable fraction, whereas, at high pH, specific sorption caused by complexation between Cu^{2+} and surface ligands in soils played a dominant role in Cu sorption, and is difficult to be desorbed by salt solution.

In the treatments with Chinese milk vetch, pig manure, and peat, formation of complexes with high binding energy might be contributed to the decrease of desorption of sorbed Cu^{2+} and Cd^{2+} [58], as compared with the control treatment. The decomposed products of these organic amendments formed complexes with Cu^{2+} and Cd^{2+} , and then, increased their specific sorption, which were difficult to be desorbed by salt solution [47], as the stability of element–organic complexes increases with soil pH [59]. Rashti et al. [53] studied Cd desorption behavior in 11 sub-tropical soils of Iran and reported the decrease of Cd desorption amounts by increasing SOM. SOM immobilized Cd^{2+} through specific sorption, resulting in the reduction of desorption of Cd [60]. Gu et al. [61] also found that incubation of red soil with Chinese milk vetch and pig manure made desorption of sorbed Cu^{2+} and Cd^{2+} more difficult than the control treatment.

Similar to the sorption, the change of desorption of sorbed Cu²⁺ and Cd²⁺ in the amendment treatments might be associated with the existing fractions of Cu and Cd in soils. Metal ions could be transformed to nonexchangeable fractions by forming complexes with soil components such as carbonate and Fe–Mn oxides by specific sorption [52]. Those metal fractions cannot be desorbed by neutral salt solutions used in this study, which resulted in the decrease of desorption of sorbed Cu²⁺ and Cd²⁺. Helios-Rybicka and Wójcik [48] also reported that the desorption of Cd by three mining wastes was associated with metal existing fractions, and the mining waste with more carbonate-bound and Mn oxides-bound (easily reducible) Cd showed less desorption percentage of Cd.

Sorption and desorption of heavy metals on soil surfaces control their concentrations in soil solution and affect their availability to crops [11, 12]. Application of the same amendments used in this study decreased Cu and Cd concentrations in soil solutions, roots, straw, and grains of rice [18] probably resulting from the increase of Cu and Cd sorption by the amendments (Fig. 1). Therefore, those amendments can decrease the bioavailability and ecotoxicity of Cu and Cd by affecting their sorption and desorption in the acid paddy soil. The effects of soil amendments on the sorption and desorption of heavy metals may be useful for predication of their efficiency in remediation of heavy metal contamination in soils. However, the batch experiments used to study heavy metals sorption and desorption by soils were usually focused on the short-term evaluation, many conflicting results about it had been reported with addition of amendments to soils [50, 62, 63]. Therefore, more studies should be conducted to evaluate the long-term effects of soil

amendments on heavy metals immobilization and release in contaminated soils.

5 Concluding remarks

The results presented in this study revealed that application of limestone, silicon fertilizer, Ca-Mg-P fertilizer, Chinese milk vetch, pig manure, and peat led to an increase in sorption of Cu²⁺ and Cd²⁺, and limestone and silicon fertilizer demonstrated higher efficiencies compared to the other amendments. The sorption of Cu²⁺ and Cd²⁺ was well fitted with the Langmuir, Freundlich, and Temkin equations. The Freundlich equation represented the best fit to the experimental data. The amount of sorbed Cu²⁺ and the increase of Cu²⁺ sorption induced by the amendments were much greater than those of Cd²⁺. Moreover, amendments decreased desorption of sorbed Cu²⁺ and Cd²⁺. Soil pH was the most important factor in controlling metal sorption and desorption. Application of amendments increased soil pH, enhanced both electrostatic and specific sorption of Cu²⁺ and Cd²⁺, and therefore, decreased desorption of sorbed Cu²⁺ and Cd²⁺. The decomposed products of organic amendments might also play an important role in affecting sorption and desorption of Cu^{2+} and Cd^{2+} in the study soil. In addition, changes of Cu and Cd existing fractions in soils with soil amendments applied might be associated with sorption and desorption of Cu²⁺ and Cd²⁺. These results demonstrated that soil amendments may be effective to immobilize Cu and Cd by affecting their sorption and desorption in contaminated soils, and further studies should be conducted to evaluate their long-term effects.

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