CADMIUM SORPTION CHARACTERISTICS OF SOIL AMENDMENTS AND ITS RELATIONSHIP WITH THE CADMIUM UPTAKE BY HYPERACCUMULATOR AND NORMAL PLANTS IN AMENDED SOILS

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*In order to select appropriate amendments for cropping hyperaccumulator or normal plants on contaminated soils and establish the relationship between Cd sorption characteristics of soil amendments and their capacity to reduce Cd uptake by plants, batch sorption experiments with 11 different clay minerals and organic materials and a pot experiment with the same amendments were carried out. The pot experiment was conducted with *Sedum alfredii* and maize (*Zea mays*) in a co-cropping system. The results showed that the highest sorption amount was by montmorillonite at 40.82 mg/g, while mica was the lowest at only 1.83 mg/g. There was a significant negative correlation between the *n* value of Freundlich equation and Cd uptake by plants, and between the logarithm of the stability constant *K* of the Langmuir equation and plant uptake. Humic acids (HAs) and mushroom manure increased Cd uptake by *S. alfredii*, but not maize, thus they are suitable as soil amendments for the co-cropping *S. alfredii* and maize. The stability constant *K* in these cases was 0.14–0.16 L/mg and *n* values were 1.51–2.19. The alkaline zeolite and mica had the best fixation abilities and significantly decreased Cd uptake by the both plants, with *K* ≥ 1.49 L/mg and *n* ≥ 3.59.*

KEY WORDS: clay minerals, organic materials, heavy metals, sorption constants, *Zea mays*, *Sedum alfredii*

INTRODUCTION

Heavy metal pollution of croplands in China has recently intensified due to mining activity, and the application of sewage sludge and heavy metal-containing fertilizers. This has resulted in a significant challenge for food security and ecological safety in China (Chen *et al.* 2000).

At present, remediation methods for heavy metal contaminated soil include physical, biological and chemical treatments. Among them, *chemical remediation* typically employs

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soil amendments which can reduce their bioavailability through a variety of reactions. The technology relies on choosing an economic and effective *amendment* (Mercier and Detellier 1995). Many scientists have studied the adsorption of heavy metals on clay minerals including zeolite, sepiolite, attapulgus, illite, montmorillonite and other natural clay minerals or modified forms, and have found that they have great potential to remove heavy metals from water (Liu and Gonzalez 1999; Liu 2007; Missana, Gutierrez, and Alonso 2008; Bailey *et al.* 1999; Gworek 1992a, 1992b). These clay minerals are low cost materials and offer an attractive and inexpensive remediation option. They are abundant and cheap, with negatively charged layered aluminosilicates that make them good cationic adsorbents because of their relatively large surface areas (Wu *et al.* 2009). In recent years, researchers have used clay minerals in the remediation of heavy metal contaminated soil and achieved positive results (Haidouti 1997; Zorpas *et al.* 2000; Nissen, Lepp, and Edwards 2000; García-Sánchez, Alastuey, and Querol 1999).

Organic amendments have also been used in the remediation of heavy metal contaminated soils (Herwijnen *et al.* 2007). Application of organic matter in forms such as *cattle manure*, pig manure, chicken manure, peat and crop straw are inexpensive, highly available and feasible in the restoration of heavy metal contaminated soils. It was shown by Sauvé *et al.* (2003) that the adsorption ability of heavy metals on soil organic matter is 30 times that of the clay minerals, so soils with high *organic matter content* had a higher *adsorption capacity* and could effectively reduce the mobility of heavy metals. The stability of the complex will influence the bioavailability and extraction of heavy metals by plants. In addition, the organic materials can affect the acidity and redox properties of the soil (Walker *et al.* 2003; Walker, Clemente, and Bernal 2004). Although in-situ remediation with *amendments* for heavy metal contaminated soils is widely studied, the impact of OM on the element retention is case specific and generalizations are difficult to make (Kumpiene, Lagerkvist, and Maurice 2008). The relationship between the sorption characteristics of soil amendments and subsequent effects in reducing plant uptake *has not been established*.

Among common remediation methods of heavy metal contaminated soils, *phytoremediation* has the advantages of *in situ remediation*, *low cost*, and the retention of soil biological function (McGrath, Zhao, and Lombi 2002). Conversely, it presents disadvantages including the problem that the *hyper accumulators* often have a small biomass and thus low extraction rate, and so a long time is required for soil clean up. Therefore some studies have used natural and/or synthetic chelators such as EDTA, EGTA, EDDS to increase the uptake and translocation of heavy metals from soil, thus achieving higher removal rates (Doong, Wu, and Lei 1998; Tandy *et al.* 2004; Zheng *et al.* 2007). Unfortunately, most of these chelators showed some negative effects to the soil environment such as elevated toxicity to both plant and the groundwater. Therefore, it is crucial to develop a method to enhance phytoremediation efficiency and minimize adverse effects. Alternatively, some researchers proposed a co-crop system of a *hyperaccumulator* with a low metal crop, which ensures production of animal feeds whilst remediating the soil (Liu, Wu, and Banks 2005; Wu, Wei, and Ouyang 2007). In this system, animal manure applications are required with successive croppings to maintain the crop yield, but the application of amendments should ideally not decrease the metal uptake by the co-planted *hyperaccumulator*.

A pot experiment was conducted in this study to screen for environmentally friendly and low cost soil amendments which will not inhibit the remediation efficiency of *Sedum alfredii* yet reduce metal uptake by co-cropped maize. Sorption experiments of Cd on the same soil amendments were also conducted. The results from both experiments will

provide probably suitable sorption parameters which can help in predicting the effects of amendments on *phytoavailability* of heavy metals for two different plants in amended soil.

MATERIALS AND METHODS

Materials

Kaolinite, montmorillonite, zeolite, diatomite, and micas were obtained from Guangying Co. LTD (Guangdong province, China). Pigmanure, chickenmanure, wormcast, mushroom residue and peatwere purchased from the Xuneng Biotechnology Co. LTD (Guangdong province, China). Humicacids (HAs, secondgenerationproduct) were obtained from Wanguo Biochemical Group R&D Center (Hebei province, China). All other chemicals used in this study (NaNO_3 , $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, HNO_3 and NaOH) were analytical reagent grade. Stock solution of Cd^{2+} was prepared by dissolving cadmium nitrate in deionized water. The characteristics of the clay minerals and organic materials are shown in Table 1.

Heavy metal contaminated soil was collected from 0–20 cm in Shangba, an agricultural field adjacent to a mine in Shaoguan in the Guangdong province of China. The basicphysiochemicalproperties and total contents of nutrients and heavy metals of the soil were as follows: clay (<0.001 mm) 250 g/kg, pH 4.43, CEC 3.3 cmol/kg, organic matter 15.7 g/kg, N 1.37 g/kg, P 0.58 g/kg, K 16.2 g/kg, Cd 0.69 mg/kg, Zn 355.7 mg/kg, Pb 512.4 mg/kg and Cu 517.7 mg/kg. The soil parameters were determined using the methods proposed by the Soil Science Society of China (Lu 2000). For determining the total contents of heavy metals, the soil samples were digested using HNO_3 , HF, HClO_4 in the ratio 5:5:3 (Lu 2000) and the concentrations of heavy metals in the solutions were determined by Atomic Absorption Spectrometry (AAS) (Hitachi Z-2300, Z-2700).

The Cd/Zn hyperaccumulator used was *Sedum alfredii*, which was collected from an old Pb/Zn mine area in Zhejiang province, China. The crop plant used was maize (*Zea mays*, CV. Yunshi-5) which was obtained from the Chunxi SeedIndustry (Yunnan province, China).

Table 1 Chemical characteristics of the clay minerals and organic materails used as amendments in this study

	Cd (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Total N (g/kg)	Total P (g/kg)	Total K (g/kg)	Organic Matter (g/kg)	pH
Mushroom manure	0.275	2.38	11.27	48.14	25.10	2.07	22.27	416.1	4.72
Humic acids (HAs)	0.073	19.46	78.56	86.94	10.33	0.51	14.32	387.2	4.31
Wormcast manure	1.949	57.91	226.1	546.0	22.79	8.44	27.90	460.3	4.78
Pig manure	1.409	11.33	41.64	112.8	25.55	5.07	22.07	434.3	4.69
Chicken manure	0.563	13.22	62.69	160.6	47.28	3.99	19.93	425.5	4.55
Peat	0.230	9.49	68.55	70.19	18.58	3.90	22.13	417.2	4.77
Kaolinite	0.057	30.54	8.36	32.51	0.00	0.18	4.48	0.17	3.58
Mica	0.058	3.02	1.11	7.67	0.00	0.24	2.27	0.06	9.46
Zeolite	0.706	2.95	1.71	15.34	0.00	0.04	2.44	0.86	9.73
Diatomite	0.121	9.47	12.34	42.20	0.00	0.67	5.05	1.48	5.64
Montmorillonite	0.236	43.86	3.36	59.13	0.00	0.14	8.13	2.09	6.33

Sorption Tests

According to the method of Kooner *et al.* (1992), sorption tests were performed by batch technique in three replicates. 0.125 g of the adsorbent was weighed into 100 mL centrifuge tubes containing 25 mL of known concentration of Cd^{2+} solution (0.4–160 mg/L, 9 concentrations). The experiments were conducted with 0.01 mol/L NaNO_3 as the background electrolyte and the pH was adjusted to 5.0 by 0.1 M NaOH or 0.1 M HNO_3 . The suspension was shaken at 160 rpm for 24 h at 25°C. After centrifugation at 5000 rpm for 10 min, the concentration of Cd^{2+} in the supernatant was analyzed with AAS (Hitachi Z-2300, Z-2700). The amount of Cd^{2+} adsorbed was calculated by the difference between the amount of Cd^{2+} added and that remaining in the solution.

Pot Experiment

The pot culture was conducted in a greenhouse at the South China Agricultural University. The soil samples were air dried and ground to pass through a 5 mm sieve. A total of 5 kg of dry soil was used in each pot ($19 \times 21 \times 23 \text{ cm}^3$). Eleven different amendments were separately added to the soil at the same level (50 g/pot). A control without amendment was also set up. In order to avoid the variability of soil fertility, all 12 treatments were fertilized with 100, 100 and 80 mg N, K and P per kg soil, respectively (added with urea and KH_2PO_4).

Seeds of maize were sterilized in 2% (v/v) hydrogen peroxide for 15 min, washed with tap water and soaked in water for one day, then sowed directly into prepared soils in October 2011. Five seedlings of *S. alfredii* (5 cm in height) were transplanted into each pot. After three weeks, maize seedlings were thinned to one seedling per pot. Tap water was added throughout the experiment to sustain 60% water holding capacity. Each treatment was performed in four replicates. Maize was harvested after reaching maturity (100 days) and *S. alfredii* one week later.

Determination of Plant Heavy Metals

The plant tissues were dried at 65°C for 76 h to obtain the dry weights. The oven dried materials were finely ground in an agate mill. The plant samples were incinerated smokelessly on a hotplate and placed in a muffle furnace at 550°C for 5.5 h. The dry ash was then dissolved by 2 mL of 1:1 (v:v) HCl and adjusted to a final volume of 25 mL for total metal analysis. The concentrations of Zn, Cd and Pb were determined with AAS.

Statistical Analysis

The means and standard deviations (SD) were calculated by Microsoft Office Excel 2003. The sorption isotherm simulation was conducted with Origin 7.05. Analysis of variance and comparison between means by Duncan's test were carried out with SAS 8.1 (SAS Institute Inc., Cary, NC, USA) (Hong and Hou 2004).

RESULTS

Sorption Isotherms

Table 2 shows parameters determined from the sorption isotherms of Cd^{2+} on the various clay minerals and organic materials. The sorption data were fit with the Langmuir

(1) and Freundlich (2) models:

$$Q_e = Q_m C_e / (1/K + C) \quad (1)$$

$$Q_e = K_f C_e^{1/n} \quad (2)$$

Where Q_e is the adsorbed amount on adsorbent (mg/g), C_e is the concentration of metal ions in solutions at equilibrium (mg/L), Q_m is the maximum sorption capacity, K is the sorption stability constant (L/mg); K_f and n are Freundlich constants.

The sorption parameters obtained from the two models (Table 2) showed that the Freundlich model did not fit the Cd sorption data for the amendments as well as the Langmuir except for kaolinite and diatomite. However, the Freundlich equation displayed a wide adaptability with significant correlations for all amendments. Maximum sorption amount of Cd^{2+} , was highest for montmorillonite at 40.82 mg/g, followed by pig manure and wormcast manure at 37.04 mg/g and 36.10 mg/g, respectively. The lowest was mica at 1.83 mg/g.

Many studies have reported the sorption of Cd^{2+} on organic materials and clay minerals. Wu *et al.* (2011) studied the sorption ability of Cd^{2+} from aqueous solutions on humic acid modified Ca-montmorillonite, and the results showed that the Langmuir model provided a better fit for adsorption of Cd^{2+} on the modified clay than the Freundlich model, as well as for the adsorption of Cd^{2+} by the raw clay. Karapinar and Donat (2009) reported the Langmuir model effectively described the sorption data of Cd^{2+} on bentonite with R^2 values >0.99 with the maximum adsorption of 7.64 mg/g (0.068 mmol/g). However, Gupta and Bhattacharyya (2006) reported that the adsorption of Cd^{2+} on kaolinite and montmorillonite was well fitted with both the Langmuir and Freundlich isotherms (R^2 values of >0.96). Ibrahim *et al.* (2010) showed similar results for zeolites prepared from local Egyptian clay (kaolin). Safa *et al.* (2012) studied the adsorption of Cd^{2+} from aqueous solution by Algerian raw diatomite and the results showed that the adsorption equilibrium was well described by both model isotherms, while the maximum adsorption capacities reached 20.2 mg/g (0.18 mmol/g). Moreover, Kalmykova *et al.* (2008) investigated the adsorption of metal ions on *Sphagnum* peat and the results showed the adsorption data fitted the Freundlich equation with $R^2 >0.96$. Zhu *et al.* (2008) studied the adsorption

Table 2 Simulated parameters of Cd^{2+} adsorption on soil amendments by the Langmuir and Freundlich isotherm models. (25°C, 9 Cd concentrations; significant R value = 0.666)

Treatment	Langmuir: $Q_e = Q_m C_e / (1/K + C)$			Freundlich: $Q_e = K_f C_e^{1/n}$		
	R	Q_m (mg/g)	K (L/mg)	R	K_f	n
Mushroom manure	0.994	30.49	0.14	0.971	2.95	1.51
Humic acids (HAs)	0.994	16.47	0.16	0.979	2.39	2.19
Wormcast manure	0.997	36.10	0.21	0.971	4.37	1.47
Pig manure	0.997	37.04	0.20	0.963	4.75	1.42
Chicken manure	0.997	30.67	0.25	0.975	4.57	1.68
Peat	0.996	32.79	0.23	0.984	5.29	1.81
Kaolinite	0.593	—	—	0.993	0.02	0.97
Mica	0.999	1.83	1.49	0.967	0.64	3.60
Zeolite	1.000	18.42	33.94	0.754	14.24	5.72
Diatomite	0.875	5.35	0.01	0.991	0.10	1.47
Montmorillonite	0.992	40.82	0.45	0.880	13.08	2.34

behavior of Cd^{2+} on pig manure and wormcast manure, and found that the adsorption isotherm conformed to the Freundlich and Henry equations, and a much higher adsorption capacity of Cd^{2+} was found in wormcast manure than in pig manure. Compared to these studies, the results of the present experiment are normal.

Effects of Soil Amendments on Plant Growth and Soil pH

Table 3 illustrates the effects of amendments on soil pH and maize biomass. At the end of the experiment, no significant change in soil pH was detected for amended soils except in those treated with zeolite and mica. The soil pH in the alkaline zeolite and mica treatments increased by 3.07 and 2.76 compared to the control. Soil pH is considered to be one of the most important chemical factors controlling the availability of heavy metals (Li *et al.* 2011). The increase in soil pH could decrease the phytoavailability of the soil. Zhang *et al.* (2006) found that soil pH increased by 1.2 with addition of manures. The results of this experiment showed only a 0.04–0.29 pH increase with the application of organic materials.

Maize grain production among treatments of mushroom manure, humic acids, wormcast manure, pig manure, chicken manure, peat soil, mica and zeolite were significantly higher than that of the control (Table 3). Grain production increased 47.9%, 35.4%, 73.5%, 84.5%, 87.6%, 74.0%, 92.7%, and 70.1%, relative to the control, respectively. Maize straw biomasses among soils treated with wormcast manure, chicken manure, mica, peat and zeolite were significantly higher compared with the control (16.7–53.4% higher than control). This suggests that organic materials can effectively promote the growth of maize in this Cd treated soil and that maize grain and straw biomass can increase with the application of organic materials, especially maize grain. Liu *et al.* (2009) also reported that chicken manure compost significantly increased wheat seed yield in Cd treated soils. For the clay minerals, only the alkaline mica and zeolite treatments significantly increased maize yield, probably due to the pH increase, which was more suitable for the growth of maize than the non-amended soil.

Effects of Soil Amendments on Cd Uptake by Maize

The applications of amendments did not significantly decrease the Cd content of maize grain (Table 3). In fact, mushroom manure, HAs, pig manure and diatomite amendments increased grain Cd compared with the control. However, the Cd concentrations in maize grain for all the treatments were still below the limit required by the Chinese food standards (GB 2762-2005).

It was found that mushroom manure, HAs, mica and zeolite significantly diminished Cd concentration in maize straw compared with the control (Table 3), by 32.3%, 24.7%, 56.9%, and 53.0%, respectively. This indicates that the translocation of Cd from maize straw to grain may be increased with the application of HAs and mushroom manure, similar to the study of Wang *et al.* (1999) who reported that rice straw and Chinese mile vetch promoted the transport of Cu from straw to grain of rice. The other amendments did not significantly decrease Cd concentrations in maize straw.

The results showed that the total uptake of Cd significantly decreased in the mica and zeolite treatments compared with that of control, while it significantly increased in the chicken manure and diatomite treatments (Table 3).

Table 3 Final soil pH, biomass production and Cd uptake by maize in response to application of different amendments

	Soil pH	Biomass (g/pot)		Cd		
		Maize grain	Maize straw	In grain (mg/kg)	In straw (mg/kg)	Total uptake (ug/pot)
CK	4.29 ± 0.14bc	49.88 ± 8.23de	124.8 ± 11.96cd	^a 0.027 ± 0.005cde	1.036 ± 0.148abcd	29.41 ± 0.69bc
Mushroom manure	4.58 ± 0.11b	73.77 ± 12.73bc	153.0 ± 14.10abc	0.043 ± 0.009ab	0.701 ± 0.147f	26.14 ± 5.38c
Humic acids (HAs)	4.33 ± 0.22bc	67.54 ± 11.28c	136.9 ± 24.67bcd	0.042 ± 0.008ab	0.78 ± 0.139ef	26.58 ± 1.46c
Wormcast manure	4.50 ± 0.30bc	86.52 ± 16.98ab	191.2 ± 20.82a	0.033 ± 0.008bcd	0.843 ± 0.053def	32.12 ± 5.03abc
Pig manure	4.36 ± 0.07bc	92.03 ± 9.25a	144.6 ± 9.48bcd	0.042 ± 0.008ab	1.149 ± 0.215abc	35.98 ± 2.85ab
Chicken manure	4.39 ± 0.28bc	93.55 ± 4.91a	171.1 ± 12.86ab	0.035 ± 0.007bcd	1.033 ± 0.191abcd	39.39 ± 6.90a
Peat	4.42 ± 0.21bc	86.76 ± 7.86ab	164.6 ± 10.89ab	0.029 ± 0.007cde	0.935 ± 0.097cde	33.57 ± 2.50abc
Kaolinite	4.24 ± 0.05bc	35.96 ± 2.76e	107.12 ± 47.76d	0.033 ± 0.008bc	1.252 ± 0.207a	37.17 ± 7.68ab
Mica	7.05 ± 0.63a	96.13 ± 5.31a	172.3 ± 8.64ab	0.020 ± 0.004e	0.447 ± 0.041g	16.84 ± 1.88d
Zeolite	7.36 ± 0.08a	84.85 ± 17.56ab	173.9 ± 54.97ab	0.023 ± 0.006de	0.487 ± 0.024g	17.98 ± 4.23d
Diatomite	4.19 ± 0.05bc	64.87 ± 6.38cd	145.5 ± 5.81bcd	0.049 ± 0.005a	1.212 ± 0.128ab	39.84 ± 4.34a
Montmorillonite	4.15 ± 0.05c	60.37 ± 15.68cd	142.5 ± 18.61bcd	0.035 ± 0.007bc	1.023 ± 0.108bcd	35.12 ± 8.04ab

All data are means ± standard error.
Means with different letters within each row are significantly different at $p < 0.05$.
Foodstandards in China (GB 2762-2005): Cd: 0.1 mg/kg; Zn: 50 mg/kg; Cu: 10 mg/kg; Pb: 0.2 mg/kg.

It appears that application of mica and zeolite can greatly decrease Cd phytoavailability in soil by decreasing not only its uptake by maize, but also the Cd contents in grain and straw. Mushroom manure and HAs can decrease Cd in maize straw and the uptake by maize but may increase the translocation of Cd to grain. Diatomite can increase Cd phytoavailability in the tested soil indicated by increased Cd total uptake by maize and Cd contents in straw and grain.

Effects of Amendments on the Phytoextraction Rate of Heavy Metals by *Sedum alfredii*

Table 4 shows the effect of amendments on the phytoextraction rate of Cd and Zn by *S. alfredii*. Compared to the control, phytoextraction rate of Cd significantly increased by 47.5% and 48.5% in the mushroom manure and HAs treatments, respectively while the mica and zeolite treatments significantly decreased by 80.5% and 83.2%, respectively. The other amendments did not significantly influence the phytoextraction rate.

S. alfredii is also a hyperaccumulator of Zn. The phytoextraction rate of Zn was significantly increased by HAs, similar to Cd, but Mushroom manure did not have a significant influence on Zn phytoextraction. Mica and zeolite significantly decreased the phytoextraction of Zn by *S. alfredii*.

Relationship Between Cd Sorption Constant on Amendments and Plant Uptake

Significant negative correlations were found between Cd concentration in maize grain and isotherm model components, n (Freundlich) and K (Langmuir; Figure 1). Similar trends were observed for Cd concentration in maize straw (Figure 1). Cadmium phytoextraction rate for *S. alfredii* was also significantly and negatively correlated with n and $\log K$ (Figure 2). Nevertheless, the maximum sorption capacity ($Q_{\max}$) predicted by the Langmuir isotherm and the K_f constant from the Freundlich isotherm did not significantly correlate with Cd in maize, or with *S. alfredii* phytoextraction rate. Therefore, the effect of amendments on

Table 4 Phytoextraction rate of Cd and Zn by *Sedum alfredii* among soils treated with different amendments

Treatment	Cd (%)	Zn (%)
CK	13.26 ± 0.91bc	2.693 ± 0.29bc
Mushroom manure	19.55 ± 3.66a	2.858 ± 0.26bc
Humic acids (HAs)	19.69 ± 1.35a	3.475 ± 0.38a
Wormcast manure	10.65 ± 1.99c	1.776 ± 0.35d
Pig manure	13.924 ± 2.25bc	2.408 ± 0.08c
Chicken manure	15.95 ± 3.09b	2.501 ± 0.10c
Peat	15.28 ± 1.93b	2.469 ± 0.11c
Kaolinite	13.96 ± 0.58bc	3.071 ± 0.41ab
Mica	2.589 ± 0.50d	0.372 ± 0.04e
Zeolite	2.225 ± 0.29d	0.317 ± 0.02e
Diatomite	12.73 ± 2.67bc	2.785 ± 0.47bc
Montmorillonite	12.67 ± 2.53bc	3.087 ± 0.52ab

Phytoextraction rate = Cd amount phytoextracted by plant/Cd amount in soil.

All data are means ± standard errors.

Means followed by different letters within each row are significantly different at $p < 0.05$.

Figure 1 Correlations between Cd concentrations in maize and sorption stability constants generated from Freundlich (n) and Langmuir isotherms (K) for soil amendments (The horizontal lines represent the intervals of the mean Cd concentration of the control without amendment. One * and two ** indicate significant at probability 95% and 99% for the correlation).

Cd uptake by plants seems related to the stability or energy constants of sorption, which provides a useful tool.

Figure 1 shows that there were four amendments that could significantly decrease Cd in maize straw, but only two amendments significantly decreased Cd phytoextraction by *S. alfredii* (Figure 2 and Table 4; alkaline mica and zeolite). Alkaline mica and zeolite produced an $n \geq 3.59$ and $K \geq 1.49$ L/mg ($\log K \geq 0.17$) (Table 2). Amendments that were amendments in adsorption effectiveness were mushroom manure and HAs (Table 3), with n ranging from 1.51 to 2.19, and K from 0.14 to 0.16 L/mg (Table 2).

DISCUSSION

In the sorption procedure, the Cd-amendment solutions were initially adjusted to pH 5, as suggested by Kooner *et al.* (1992), but the solution pH was not maintained. The measured pH after the sorption equilibrium was 6.18–6.85 and 6.36–7.17 for mica and zeolite, respectively, which was similar to the amended soil (Table 3). This may also partly simulate the real effect of the amendment on soil pH and might be good for predicting the behavior of the amendment in soil. Under this condition, The degree of sorption was partly due to the precipitation of Cd. Therefore, the sorption constants obtained from the study were the result of precipitation and adsorption. Similar effects have been described in the

Figure 2 Correlations between the Cd phytoextraction rates by *Sedum alfredii* and sorption stability constants of soil amendments simulated by the Freundlich (n) and Langmuir (K) isotherm models (The horizontal lines represent the intervals of the mean Cd phytoextraction of the control without amendment. One * and two ** indicate significant at probability 95% and 99% for the correlation).

literature, for example, Sastre *et al.* (2006) pointed out that metal precipitation should not be disregarded in the processing of adsorption process.

The alkaline zeolite and mica were found to be effective for normal crops in this study since they were able to significantly decrease Cd phytoavailability in the studied acid soil. The other amendments including all organic amendments could be used for cropping the hyperaccumulator if necessary. In particular, soil amendments possessing Freundlich n values between 1.51 and 2.19 ($0.14 \leq K \leq 0.16$ L/mg) such as HAs and mushroom manure can reduce the Cd concentration in maize straw but not phytoextraction of Cd by *S. alfredii*, making them suitable for co-cropping. Chicken manure and diatomite are not suitable for cropping maize on Cd contaminated soils, because they may increase the uptake of Cd

(Table 3). Diatomite had a very low stability constant ($K = 0.01 \text{ L/mg}$), which explains the lack of ability to decrease Cd uptake. However, the increase in Cd uptake with amendment of chicken manure cannot be explained by a low sorption stability constant. The involved mechanisms need to be elucidated.

CONCLUSION

The maximum Cd sorption capacity for montmorillonite (40.82 mg/g) was the highest among all studied amendments, followed by pig manure (37.04 mg/g) and wormcast manure (36.10 mg/g). Mica had the lowest Cd sorption at 1.83 mg/g. The n value fitted by the Freundlich equation and the logarithm of equilibrium constant K fitted by the Langmuir equation presented a significant linear negative correlation with Cd uptake by plants. At an application rate of 10 g/kg in a co-cropping system, HAs and mushroom manure increased the Cd uptake in *S. alfredii*, but not in maize, thus are suitable for the co-crop system. Alkaline zeolite and mica had the highest fixation ability and decreased Cd uptake by both *S. alfredii* and maize and had a K value of $\geq 1.49 \text{ L/mg}$ and $n \geq 3.59$. These amendments are good for cropping maize, but not suitable for cropping the hyperaccumulator. These sorption indicators are helpful to choose the appropriate amendments for different crops in contaminated soils.

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