

Review

# Influence of pH on the Particulate-Bound Cd Speciation and Uptake by Plants

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## Abstract

The speciation of heavy metals in soil is a better indicator for assessing the bioavailability than the total concentration. Soil pH is a vital factor influencing the particulate-bound metal speciation and the metal dynamics at rhizosphere soil-root interface. In this study, greenhouse pot experiment was conducted to reveal the influence of pH on the speciation of cadmium (Cd) in solid phase of soil and the amount of Cd uptake by different ecotype plants. The results illustrated that the exchangeable Cd decreased obviously with the increase of soil pH, while the residual Cd displayed the reverse. The amount of Cd uptake by plants increased with pH decreased, and pH 5.5 exhibited the optimum for plants growth and metal uptake. Furthermore, the biomass and uptake capability of the hyperaccumulator plants (*Sedum alfredii* and *Beta vulgaris var. cicla L* with red leaves) were higher than the corresponding non-hyperaccumulator plants. Results indicated that the pH decrease and rhizosphere effects of hyperaccumulator could facilitate the activation of Cd and enhance the phytoremediation efficiency significantly.

**Keywords:** Cd, pH, rhizosphere, speciation, phytoremediation

## Introduction

Heavy metal contamination in soil has become a severe issue around the world in recent years as a result of anthropogenic activities [1, 2]. Cd is recognized as one of the most toxic and carcinogenic metals in soil, which may transfer from plants to human body by dietary intake exposure [3-5]. Various techniques

were available to remediate the heavy metal-polluted soil. However, the engineering-based technique is expensive, environmental-unfriendly and even generate secondary contaminates to soil [6, 7]. Phytoextraction, removal of the pollutants by cropping and harvesting the bioaccumulating plants, has been a favourite choice for remediation. Process of the phytoextraction largely depends on the bioavailability of metals and the ability of accumulation by plants [8].

Rhizosphere is a non-equilibrium millimeter micro-space environment, composed of plant roots, minerals, water, oxygen, organic matter and microorganisms [9].

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Due to the secretion of plant roots, the rhizosphere environment is always in dynamic changes of pH value, redox potential, microbial characteristics and soil enzyme activity, which will further affect the mobility and bioavailability of heavy metals [10, 11]. The specific micro-space is therefore identified as a key process for phytoextraction. Evaluating the speciation of heavy metals and their transformation in rhizosphere plays an important role in studying the fate of heavy metals. However, the processes of how various speciations were modified in rhizosphere and then uptake by accumulating plants still have not been illustrated thoroughly.

Trace metals are absorbed and retained in soil associated with soil properties, such as pH, the cation exchange capacity, the content of organic matter and clay minerals [11]. Contrast with other factors, pH was emphasized as one of the most important factors to regulate the speciation and bioavailability of metals in the solid-liquid phase of soil [12]. A broad range of pH existed in the natural environment, such as the acidic soil of 4.0-5.5 in East China, and the alkaline soil between 8.0-8.5 in Tianjin and other regions in North China [13]. Wang et al. [14] investigated that soil available Cd was negatively correlated with the pH value with additives application in acidic soil. Shen et al. [12] pointed out pH is the most important factor affecting the speciation of heavy metals in rhizosphere soil, and also regulating their migration in soil-plant system. Plant uptake and the speciation of heavy metals were pH-dependent and the effect of pH on the latter was significant [15]. It should be noted that both surface-charge characteristics and the concentration of other main ions are important factors regulating the sorption process at lower pH [16]. In this study, more data were provided on optimizing the remediation efficiency of bioaccumulators by changing soil pH. Pot experiments were conducted to compare the effects of different soil pH on the biomass, accumulation and removal of Cd by two different species of *Sedum* and *Beta vulgaris* L. Two ecotypes were included in each species, which were the hyperaccumulator plants *Sedum alfredii* (*S. alfredii*) and *Beta vulgaris* var. *ciela* L with red leaves (*R. Beta vulgaris*), and the corresponding non-hyperaccumulator plants *Sedum sarmentosum* (*S. sarmentosum*) and *Beta vulgaris* var. *ciela* L with golden leaves (*G. Beta vulgaris*). Results can provide scientific basis for improving the phytoextraction efficiency, and further the remediation of heavy metal contaminated soil.

## Material and Methods

### Soil Samples and Pot Experiment

Soil used in this study was collected from Dapan (123.13 E, 41.67 N) near the Xi River in Shenyang, where is a region of heavy metals contaminated site for several

decades [3]. The basic physicochemical properties of the soil were analyzed, i.e., pH 6.84, CEC 17.08 cmol·kg<sup>-1</sup>, total Cd with 7.8 mg·kg<sup>-1</sup>, and the total organic matter 25.70 g·kg<sup>-1</sup>. Four pH levels were designed for different treatments, denoting as pH 4.0, pH 5.5, pH 6.8 and pH 8.5, respectively. As the original soil pH was 6.84, it was approximately regarded as pH 6.8 and the other three treatments were further adjusted by H<sub>2</sub>SO<sub>4</sub> and CaO. The pH buffer capacity was determined according to the acid-base titration curve, and the amount of H<sub>2</sub>SO<sub>4</sub> and CaO applied was calculated by using acid-base and alkali buffer capacity [6].

The base fertilizers, including (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> were applied to soil for the nutrition of N, P and K. Before pot experiment, branches of *S. alfredii* and *S. sarmentosum* were selected for the same size and pre-cultured in pollution-free soil. Plants were transplanted into pots for successive experiment until the exuberant adventitious roots (5-7 cm) grew from the stem base. Seeds of *Beta vulgaris* L. were soaked in 10% hydrogen peroxide for 5 min and evenly scattered in a soil tank with suitable nutrients. The temperature was controlled at 28°C and the humidity was 60%. When the seedlings reached 3-4 cm, the buds were transplanted for pot experiments. After transplanting plants, the soil water content was kept at 60%-70% of the maximum water holding capacity, and the temperature in the greenhouse was kept at 20-25°C. Each pot was filled with 1 kg soil and each treatment was repeated 4 times, accompanying with the blank pots. After 70 days of growth, plants were harvested and separated into root and shoot. Soil which was tightly adhering to the roots, was collected as the rhizosphere, while the soil in blank pot were regarded as bulk soil.

### Sequential Extraction Scheme for Particulate-Bound Cd Fraction

The sequential extraction method recommended by Krishnamurti and Naidu was chosen to investigate the particulate-bound Cd fraction in soil [17]. Generally, the particulate-bound Cd fraction in solid phase was operationally divided into “exchangeable”, “Specifically-adsorbed”, “organic complex-bound (fulvic acid-bound and humic acid-bound)”, “easily reducible oxide-bound”, “organic-bound”, “amorphous mineral colloid-bound”, “crystalline iron oxide-bound” and “Al-Si minerals-bound”, denoted as exchangeable, adsorbed, fulvic complex, humic complex, reducible, organic, amorphous, crystalline, and residual, respectively. The sequential extraction was carried out in duplicate and 0.5 g of each soil sample was taken in 50 mL centrifuge tubes. The supernatant was removed after centrifugation with a high-speed centrifuge (10000 g) for 10 min, and the residue was cleaned twice with 5 mL ultra-pure water for each step of extraction. After each cleaning, the supernatant was centrifuged with a high-speed centrifuge (12000 g) for 10 min, and mixed at a constant volume before the next extraction was

carried out. For the last step of continuous extraction, the residue fraction was digested with  $\text{HNO}_3$ - $\text{HClO}_4$ -HF. The concentration of Cd in the supernatant after each step of extraction was determined by graphite furnace atomic absorption spectrometry (contr AA 700).

### Statistical Analysis

All data displayed as standard deviations in this study, calculated from the replicate values of each treatment. The Tukey test was used to identify the significant differences ( $P < 0.05$ ) in means of the treatments, denoted by different letters. All figures were made using Origin 9.

## Results and Discussion

### Distribution of Particulate-Bound Cd

The speciation distribution of Cd in bulk and rhizosphere soil at different pH were shown in Fig. 1. Results denoted that the particulate-bound Cd vary greatly with different treatments. The distribution of Cd in bulk soil was as follows: exchangeable > residual > fulvic complex > organic > humic complex > amorphous > reducible > absorbed > crystalline at pH 4.0. The concentration of residual Cd increased with soil pH, while the amount of exchangeable Cd displayed the reverse. Speciation of Cd in rhizosphere soil were mainly exchangeable and residual as well, followed by fulvic complex, absorbed, humic complex and organic at different pH. Compared with bulk soil, the proportion of exchangeable Cd in rhizosphere soil of *S. alfredii* decreased by 21.2% (pH 4.0), 16.5% (pH 5.5), 8.1% (pH 7.0) and 7.9% (pH 8.5), respectively, while the residual Cd decreased by 2.9% (pH 4.0), 28.6% (pH 5.5), 15.1% (pH 7.0) and 4.6% (pH 8.5), respectively. A similar trend was observed in the rhizosphere soil of *R. Beta vulgaris* for exchangeable and residual Cd. Furthermore, the concentration of fulvic and humic complex Cd in the rhizosphere of the two accumulators were higher in comparison with bulk soil at the same pH. However, unobvious change was observed for other Cd speciation. The results speculated that the rhizosphere effects from hyperaccumulators may have effects on the distribution of Cd speciation in rhizosphere soil compared with the corresponding non-accumulators.

As an important factor affecting the speciation and bioavailability of heavy metals in soil, pH can change the adsorption site, adsorption surface and coordination performance of heavy metals [18-19]. The transformation of particulate-bound Cd in solid phase of soil is closely related to pH and the available Cd in contaminated soils significantly increases with the pH decrease [11-12]. Dai et al. [15] conducted an experiment and determined the effects of different soil pH (from 4.83 to 7.84) on *B. pilosa* phytoextracting Cd in soil. The results

demonstrated that the extractable Cd concentration in soil was significantly decreased with the increase of pH. Li et al. [20] denoted that lower pH values favored the transformation of crystalline Fe oxides into a poorly-crystallized and organically-complexed phase, which facilitates Cd accumulation in coarser aggregates and enhances Cd mobility in paddy soils. The results aforementioned were consist with this study. At lower pH, the negative charges on the surface of clay minerals, hydrated oxygen and organic matter decreased, then the soil specific adsorption of Cd reduced. This explains why the concentration of exchangeable Cd and organic complex Cd increased at pH 4.0 and 5.5, while the particulate bound-Cd with soil clay minerals, oxides and residue were the main fractions in neutral and alkaline soil. Compared with amorphous, crystalline and the organic complex-bound Cd in soil is not stable and might dissociate and release  $\text{Cd}^{2+}$  once the soil pH decreased [16]. Otherwise, the increased concentration of  $\text{H}^+$  in lower pH was apt to have competition for  $\text{Cd}^{2+}$ , so the concentration of exchangeable Cd increased and the residue Cd significantly reduced. Overall, soil acidification facilitated the transformation of relatively stable particulate-bound Cd to unstable and exchangeable Cd fractions.

Besides the acidification of soil, root exudate, including low-molecular-weight acid, polysaccharide, and other rhizosphere substances, can accelerate the dissolution of soil minerals and heavy metals in rhizosphere soil [9, 20]. One study determined that the hyperaccumulator had a certain acidification effect on the rhizosphere soil and the pH of rhizosphere was basically 0.2 lower than that in bulk soil, accompanied by the activation of Cd [15]. Li et al. [11] indicated that adjusting pH from alkaline to slightly acidic enhanced the rhizosphere effect on solubility of trace metals. The concentration of residual Cd in rhizosphere is lower than that of bulk soil, and the effect of roots in transforming residual speciation to organic-complex and other speciation might be attributed to the activation of organic acids from roots and microbes [22]. As Li et al. [23] pointed, the concentration of small molecular organic acids and weak organic complex compound, such as fulvic acid and humic acid complex Cd increased in the rhizosphere soil. They also believed that  $\text{H}_2\text{CO}_3$  released from root respiration and the organic acids in rhizosphere can promote the dissolution of carbonate Cd and reduce the iron and manganese oxides and residual fractions.

### Dry Biomass of Plants

The dry biomass of upper plants was exhibited in Fig. 2. As can be seen from the figure, the aboveground biomass of plants was significantly smaller at pH 4.0 than the other pH values (except *S. alfredii*,  $p < 0.05$ ). Compared with that of the original soil at pH 6.8, the biomass decreased by 56.1%, 33.7% and 48.3% for *S. sarmentosum*, *R. Beta vulgaris*, and *G. Beta vulgaris*,

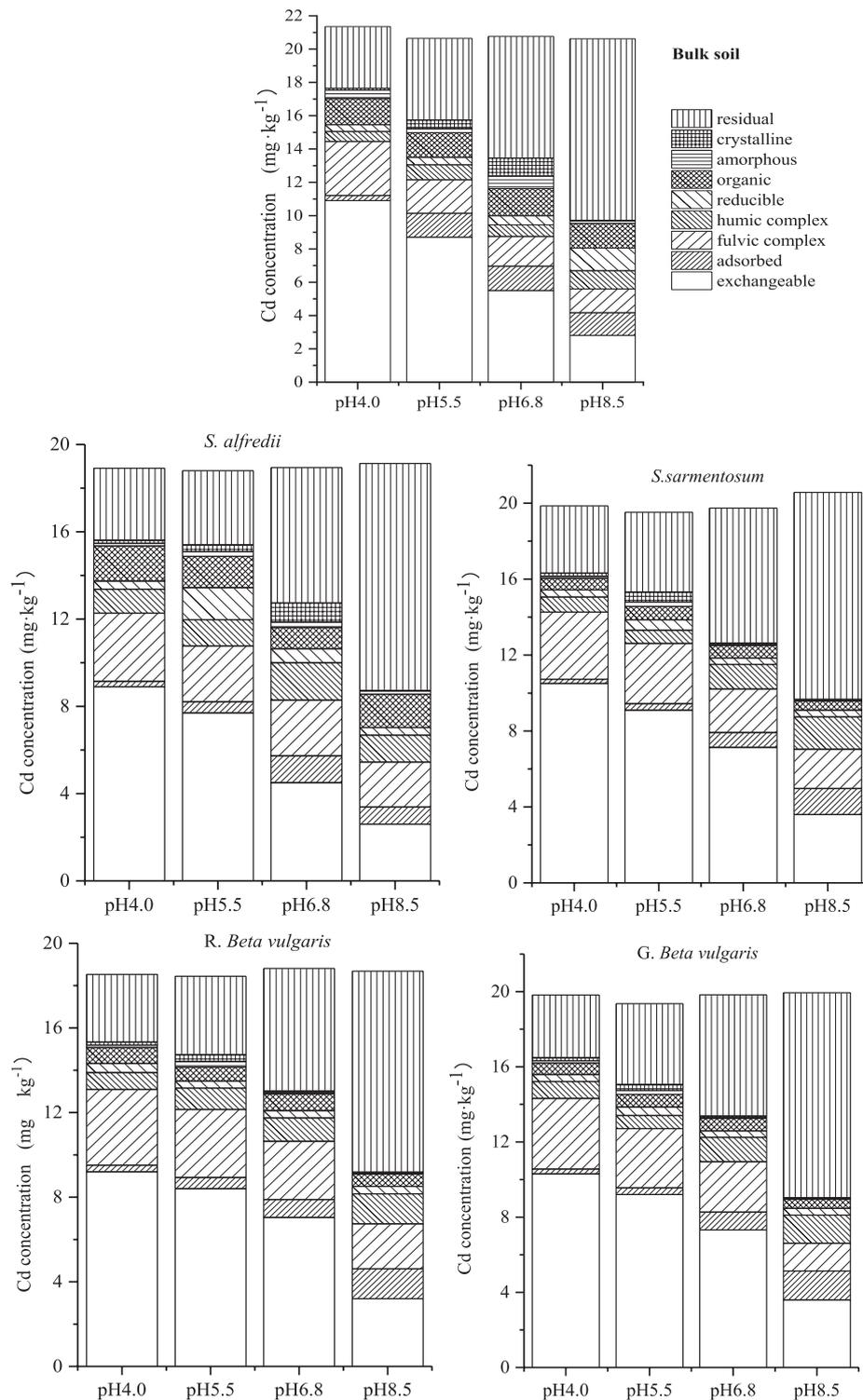


Fig. 1. Amount of Cd fraction in bulk and rhizosphere soil at different soil pH.

respectively at pH 4.0. Pot experiment also showed that plants had different degrees of withering and defoliation, with the roots obviously underdeveloped and no fine roots for this treatment, except *S. alfredii*. Compared with other plants, *S. alfredii* exhibited strong vitality characteristic during the entire growth cycle, and the dry biomass of it is always the largest at all pH, while *S. sarmentosum* is the converse.

#### Amount of Cd Uptake by Plants

The concentration of Cd uptake by plants were showed in Table 2. Results indicated that there were significant differences of Cd concentration in the four plants ( $p < 0.05$ ), during which the bioaccumulation characteristic of *S. alfredii* and *R. Beta vulgaris* were found. Concentration of Cd in *S. alfredii* significantly

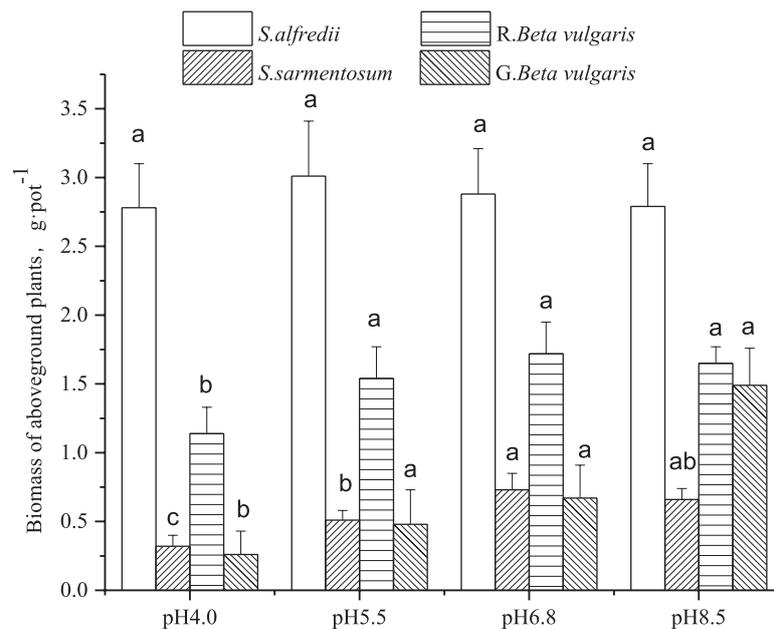


Fig. 2. Dry biomass of aboveground at different soil pH.

Different lowercase letters of the same plant indicate that the significant variation of biomass at different pH treatments ( $p < 0.05$ ,  $n = 4$ )

increased at the same pH ( $p < 0.05$ ) and denoted the admirable accumulation ability of Cd. With regard to the other non-hyperaccumulating plants, *S. sarmentosum* and *G. Beta vulgaris*, they could grow under the stress environment as well and indicated they had certain tolerance to Cd. However, their ability to accumulate Cd was obviously weaker than the corresponding hyperaccumulators. Furthermore, Cd accumulation in

the plants was higher in acidic soil than in the alkaline or neutral soil.

Our results were consistent with other studies. Dai et al. [15] showed that the Cd concentrations in *B. pilosa* were significantly higher for pH 4.83 treatment than those of pH 6.81 and 7.84 ones and the Cd concentration of *B. pilosa* grown in pH 7.84 soil was significantly lower than that in pH 6.81 soil. When soil pH increased,

Table1. Multi-step selective sequential extraction scheme for particulate-bound Cd fraction.

Step	Fractions	Reagent	Shaking time and temperature
1	Exchangeable	5 mL of 1.0 M $\text{NH}_4\text{NO}_3$ , pH 7	4 h, 25°C
2	Specifically-adsorbed	12.5 mL of 1.0 M NaOAc, pH 5	6 h, 25°C
3*	Fulvic acid- bound	15 mL of 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ , pH 10	20 h, 25°C
	Humic acid- bound		
4	Easily reducible oxide-bound	10 mL of 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ , pH 5 (in 0.01 M $\text{HNO}_3$ )	0.5 h, 25°C
5	Organic-bound	1) 2.5 mL of 30% $\text{H}_2\text{O}_2$ (pH 2), 1.5 mL 0.02 M $\text{HNO}_3$ , 2) 1.5 mL of 30% $\text{H}_2\text{O}_2$ (pH 2), 0.5 mL 0.02 M $\text{HNO}_3$ , 3) cool, 5 mL of 2.0 M $\text{NH}_4\text{NO}_3$ , pH 7 (in 20% $\text{HNO}_3$ )	2 h, 85°C 2 h, 85°C 0.5 h, 25°C
6	Amorphous mineral colloid-bound	5 mL of 0.2M $(\text{NH}_4)_2\text{C}_2\text{O}_4/0.2$ M $\text{H}_2\text{C}_2\text{O}_4$ , pH 3	4 h, 25°C (dark)
7	Crystalline iron oxide-bound	12.5 mL 0.2M $(\text{NH}_4)_2\text{C}_2\text{O}_4/0.2$ M $\text{H}_2\text{C}_2\text{O}_4$ , pH 3 (0.1M ascorbic acid)	0.5h, 95°C
8	Residual	Digestion with $\text{HNO}_3$ -HF- $\text{HClO}_4$	

\* 15 mL of 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$  extract was brought to pH 1.0 with the addition of 6 M HCl, then the suspension was left overnight for the coagulation of Humic acid. The suspension was centrifuged for 10 min (12000g), and the Fulvic acid-bound Cd was determined in the supernatant. 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$  was added to the residue and the Humic acid -bound Cd was determined in the solution.

Table 2. Concentrations of Cd in plants at different soil pH (mg·kg<sup>-1</sup>)

Treatments		<i>S. alfredii</i>	<i>S. sarmentosum</i>	<i>R. Beta vulgaris</i>	<i>G. Beta vulgaris</i>
pH 4.0	Shoot	1016.3±25.4 a A	247.4±25.2 d A	546.5±12.1 b A	124.6±5.3 c A
pH 5.5		832.5±42.3 a B	133.5±15.5 c B	295.8±14.3 b B	85.3±4.2 c B
pH 6.8		542.6±21.7 a C	92.4±8.2 d C	154.3±8.7 b B	63.7±3.4 c B
pH 8.5		314.3±22.4 a C	74.3±9.8 d D	160.4±7.2 b B	67.7±4.5 c B
pH 4.0	Root	347.1±8.9 a A	128.2±9.1 c A	103.2±9.4 b A	113.4±9.8 b A
pH 5.5		238.4±13.7 a B	164.2±10.7 c AB	78.9±4.2 bc B	89.8±8.5 b B
pH 6.8		150.1±11.6 a BC	93.8±6.3 c B	69.6±6.5 b B	52.5±4.8 c C
pH 8.5		135.5±12.2 a C	84.5±7.4 c B	87.8±3.4 b B	70.1±4.4 b BC

Different lowercase letters in the same line indicate the significant differences of plants at the same pH and the different capital letters in the same column express significant differences in the same plant under different pH ( $p < 0.05$ ).

a reduced pool of bioavailable Cd in rhizosphere soil coupled with an increased Cd retention by Fe plaque and an inhibited Cd transfer was determined, which was proposed to be largely responsible for the significant reduction of Cd in rice [24-25]. As described above, there is an inverse relationship between soil pH and the bioavailability of metals. Sun et al. [26] emphasized pH was negatively correlated with the exchangeable fraction of Cd and the accumulation in the rhizosphere soil of Little Hero Orange, Durango Yellow, and Konghuang Yellow. However, the acidity and alkalinity changing in soil had obvious effects on the growth and development of rape root system through simulated acidification tests. As withering and defoliation of the plants appeared at pH 4.0 in this study, the highest value of root activity appeared at about pH 6.1 and root system began to show signs of senescence as pH was lower than 5.8 [27]. Therefore, it should be alert that the restriction of plant growth and availability of heavy metals may simultaneously changed with pH and the reasonable level should be set with great circumspection. Furthermore, the amount of Cd accumulation in plants were attributed to the rhizosphere effects from different ecotype plants as well. Roots, especially for the *S. alfredii* in this study, can significantly alter the chemical concentration and distribution of Cd in rhizosphere soil. In comparison with other plants, the rhizosphere effects induced by hyperaccumulator *S. plumbizincicola* played an important role on the mobilization and the bioavailability of Cd, because of the larger root systems and higher acidification ability [28]. The exudation of greater amounts of DOC may also contribute to the promotion of Cd accumulation in hyperaccumulator, as denoted in our previous study and other researchers [5, 29].

### Conclusions

Soil pH and rhizosphere effects can change the particulate-bound Cd distribution in contaminated

soil. With the increase of pH, exchangeable Cd gradually decreased and the amount of residual Cd increased significantly. Compared with the bulk soil, the exchangeable Cd in the rhizosphere of the bioaccumulator decreased due to the transfer of Cd from soil to root, while the humic and fulvic complex-Cd increased as a result of rhizosphere effects. Despite the highest amount of Cd uptake at pH 4.0, pH 5.5 exhibited the optimum pH for plants growth and Cd accumulation. Furthermore, the biomass and uptake amount of Cd by *Sedum alfredii* and *R. Beta vulgaris* were higher than the corresponding non-hyperaccumulator plants *Sedum sarmentosum* and *G. Beta vulgaris*, and *Sedum alfredii* displayed the best capability. Overall, the decrease of pH and rhizosphere effects of hyperaccumulator could facilitate the activation of Cd and enhance the uptake efficiency significantly.

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### Conflict of Interest

The authors declare no conflict of interest.

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