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Research Article

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Rhizospheric effects of maize on adsorption and release of cadmium in soil: A batch sorption experiment

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ABSTRACT

Cadmium (Cd) adsorption and desorption in soils and influencing factors have well documented, however, this process in the rhizospheric environment has rarely been reported. To better understand the rhizospheric effects on the sorption of Cd in soils, the batch sorption experiments were conducted by acquisition of rhizospheric soil samples via a rhizobox culture of maize plants. Rhizospheric effects resulted in the significant enhancement of DOC and pH and reduction of Eh in rhizospheric soil. Compared with in non-rhizospheric soil, the amount of adsorbed Cd in rhizospheric soil was enhanced greatly, while the desorption of Cd was reduced. It indicated that Cd was easier to be adsorbed and more difficult to be desorbed under the rhizospheric effects. Freundrich model was the optimal equation to fit the sorption process of Cd in rhizospheric soil and in non-rhizospheric soil. The fitting results showed that the maximum and capacity of Cd adsorption was elevated greatly in rhizospheric soil. No significant difference was observed between in rhizospheric soil and in non-rhizospheric soil at the same pH in solutions, although the increasing pH promoted greatly the amount of adsorbed Cd in soils. The present results implied that the change of pH may be the primary factor inducing the enhancement of Cd adsorption in rhizosphere.

Keywords: Adsorption; Desorption; Rhizospheric effect; Cadmium; Heavy metal

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INTRODUCTION

Rhizosphere is the root-soil micro-interface, ranging usually from several microns (μm) to several millimeters (mm). Rhizosphere environment is deeply influenced by plant roots and associated microbial activity, accordingly differed from the non-rhizosphere soil in physical chemical and biological properties [1-3]. The various substances in rhizosphere released by plant roots including high- and low-molecular-weight compounds are likely to affect environmental behaviors and availability of heavy metals in soil [4].

Cadmium (Cd), as a persistent and toxic pollutant, has aroused more public concerns due to its adverse health effects to human body [5]. Cadmium in soil environments transferring into edible parts of plant by root uptake can accumulate in human bodies via food chain. Therefore, reducing the cadmium uptake by roots has been one of the focuses of environmental science. Sorption and desorption strongly affected Cd distribution between the solid and the solution phases and its bioavailability in soil [6, 7]. The sorption process of metals in soil depends on the types and property of soil, composition and pH in soil solution, and also is associated with the external anion, artificial organic and inorganic complexing agent.

Cd adsorption and desorption in soils and influencing factors have well documented, however, this process in the rhizospheric environment has rarely been reported. Taking into account the specificity of rhizosphere and its close relationship to Cd transportation in soil-plant system, it is important to study the adsorption and desorption behavior of Cd in rhizosphere soil. Based on the acquisition of rhizospheric soil of maize plant, the batch experiments were conducted in present study to investigate the adsorption and desorption processes of Cd affected by root exudates and the possible mechanism was also discussed.

EXPERIMENTAL SECTION

2 Material and methods

2.1 Incubation of rhizospheric soil

The soil used in this study was collected from Laiyang, Eastern Shandong, China. Soil properties were measured using method recommended by Lu [8]. The soil properties are listed in Table 1. A rhizobox was designed to culture maize plants according to Tao et al. A rhizobox consists of two PVC tube with different diameters as shown in Figure 1. The under part with an open top and a bottom has a diameter of 10 cm and 6 cm depth and packed with 200 g of soil. The upper part is slightly smaller with a diameter of 9 cm and a depth of 5.5 cm. The bottom of the upper part was sealed with a nylon mesh (35μm) before packing with 120 g of soil.

Table 1 Physical and chemical characteristics of selected soils

pH	Organic matter (g/kg)	CEC (cmol/kg)	Particle size (%)			Total Cd (mg/kg)
			1.0-0.05mm	0.05-0.002mm	<0.002mm	
6.76	20.24	19.38	2.48	38.45	59.07	0.09

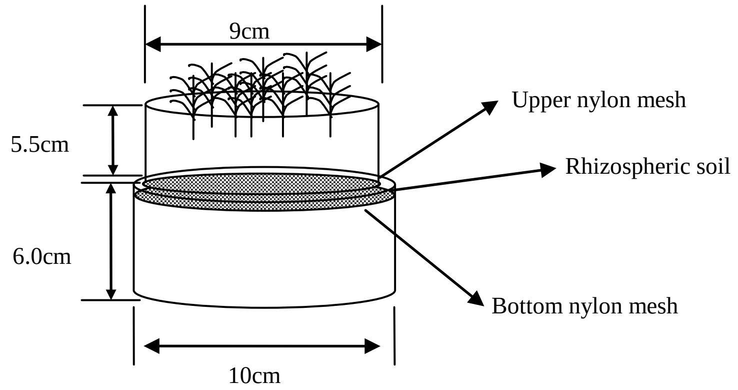

Fig. 1 Diagrammatic sketch of the rhizobox

The pre-germinated maize seeds were sown in the upper part of rhizobox. To study the various rhizospheric effects, five plants (R5) or twelve plants (R12) are cultured in each rhizobox, and no plant as the non-rhizospheric soil (NR). The box watered twice a day by weighing to keep 35% of soil moisture. When the root pad was formed after 15 d, the upper part was removed and 25.0 g of soil was added uniformly on the nylon mesh which was on the top of the under part of box. For each box, the two parts were fixed firmly with strings. The soil (25.0 g) in the two layers of nylon mesh was as the rhizospheric soil because it was in close contact with the upper root pad. The rhizobox experiments were conducted in the growth chamber at 28℃/24℃ and 14/10 day/night cycles with a relative humidity of 70-80%. The plants were harvested after 30 days. The rhizospheric soil samples were obtained for the sorption experiments and measurement of properties.

2.2 Sorption experiments

Cd sorption by each soil was determined using a batch equilibrium experiment. In the experiments of sorption isotherms, soil (1.00 g each) was weighed into 50 ml plastic centrifuge tubes containing graded levels of Cd solution. Soil suspension was shaken for 12 h at 25±1ºC using a shaker bath, and then equilibrated 6 h to ensure sorption equilibrium. After centrifuged at 5000 rpm for 10 min, the Cd concentrations in supernatant were determined. Amount of adsorbed Cd in the soils was obtained by calculating the difference between the initial and final concentrations of metals in the equilibrium solution.

Desorption experiment was conducted with the soil residue from isotherm experiment, which was washed by deionized water three times (no Cd in solution determined). The washed residue added with 1 M $NaNO_3$ solution 25 ml was shaken for 12 h at 25±1ºC in shaker bath and centrifuged for 10 min for determining Cd concentration.

The pH was adjusted by either NaOH or M HNO_3 solutions. Cd solutions was set at a uniform concentration equivalent to 10 mg/L and ionic strength of 0.01 M for each. After shaken for 12 h and equilibrated 6 h, soil suspension was centrifuged and the pH and Cd concentration in supernatant were determined.

2.3 Analysis

Soil samples were digested in mixture of HNO_3-HF-$HClO_4$. Cd concentrations of both soils and solutions were determined by AAS (AA-7000，Shimadzu，Japan). For all analysis, certified standard soil samples GBW07401 (GSS-1) were used to ensure precision of the measurement. Rhizospheric soil samples were also measured for pH, Eh and dissolved organic carbon (DOC). Soil pH was measured in a 1:2.5 soil/water suspension with a combination electrode, and the redox potential was measured with a platinum electrode. The DOC in the soil solution were determined using a TOC analyzer (TOC-V_{CPH}， Shimadzu).

RESULTS AND DISCUSSION

3.1 The properties of rhizosphere

Under the influence of maize roots, the concentrations of DOC and pH were elevated significantly in rhizospheric soil, while the Eh was reduced (Table 2). Compared with non-rhizosphere (NR), DOC concentrations were increased by 28 percent and 62 percent in R5 and R12 treatment, and pH was elevated 0.58 and 0.7 units, respectively. With the increase of amounts of plants, root biomass in soil was also promoted. The change of pH in rhizosphere may be associated with the partial pressure of CO_2 in rhizosphere, and also be affected by the selective absorption of plant [2, 10]. For xerophilous plants, the change of oxidation reductive potential (Eh) in rhizosphere is mainly caused by root respiration and microbial metabolism [11, 12]. As shown in Table 2, rhizospheric effects induced the reduction of Eh in soil at different degrees, which was 12.4 percent and 29.9 percent in R5 and R12 respectively, compared with NR. The growth of plant roots promotes the oxygen consumption in rhizospheric environment, as does the increasing microbial activity induced by root exudates [3].

Table 2 Environmental properties of soil in rhizosphere

Treatments	Biomass of maize roots (g)	DOC (mg/kg)	pH	Eh (mV)
NR	--	35.01±1.29	6.63±0.09	328.6±15.5
R5	0.59±0.04	44.81±0.84	7.21±0.14	287.8±14.1
R12	0.75±0.07	56.66±1.72	7.33±0.03	230.5±20.2

NR is non-rhizospheric soil. R5 is rhizospheric soil treated with five maize plants. R12 is rhizospheric soil treated with twelve maize plants. Values are means±S.D.

3.2 Cd adsorption and desorption in rhizospheric soils

The sorption of Cd in each soil increased with the increase of equilibrating concentration (Fig. 2). In the range of the initial Cd concentrations added in the experiment, however, the sorption plateaus were not presented for all three soils, indicating a higher capacity of the soil in Cd sorption used in the present study. Compared with the NR soil, rhizospheric soil (R5, R12) had the more amounts of absorbed Cd regardless of the initial Cd concentrations. It showed that rhizospheric effects resulted in the enhancement of Cd immobilization in soil solid. The order of adsorbed-Cd amounts in three soils was R12>R5>NR, which was in accordance with the pH and DOC and was contrary to the Eh in rhizospheric soils. The changes of soil properties induced by maize roots may be the important causes.

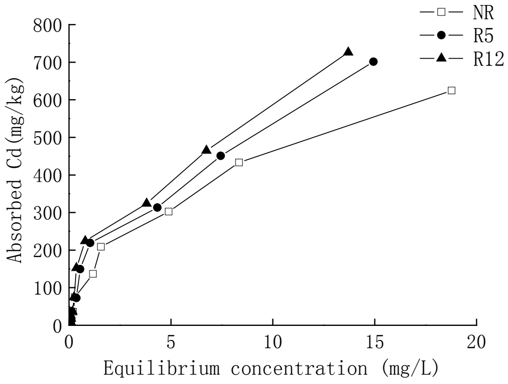

Fig. 2 Cd adsorption isotherm in soils under different rhizospheric effects.
NR is non-rhizospheric soil. R5 is rhizospheric soil treated with five maize plants. R12 is rhizospheric soil treated with twelve maize plants.

Langmuir, Freundlich and Temkin models were often applied to describe the sorption data, and the equations were shown as follows:

Langmuir：$Y=X\,a\,X_m/(1+a\,X)$

Frendrich：$Y=k\,X^{1/a}$
Temkin：　$Y=a+k\,\log X$

Where X is Cd concentration in equilibrium solution (mg/L), Y is the amount Cd absorbed (mg/kg) by the soil and X_m is the adsorption maxima. The k and a denote constants of equations. A non-linear fit method using Levenberg-Marquardt (LM) arithmetic from Microcal Origin 7.5 was conducted to fit the sorption data. The results were listed on Table 3.

According to the value R^2, which can be used to estimate fitting results, Freundrich model was the optimal equation in fitting the sorption data, while Temkin model had the poor adaptation (Table 3). According to X_m given by Langmuir model, the order of Cd maximum sorption by three soils was: R12>R5>NR. According to previous studies, pH was the most important factor to affect Cd sorption by soils. The increase of soil pH enhanced significantly the sorption of Cd by soils [13, 14]. Also, the organic matter affected greatly the process of Cd sorption by soils [15]. With the multiple linear regression analysis, Sauvé et al. considered that soil organic matter following pH was the second component significantly affected the Cd sorption [16]. In the present study, the enhancement of pH and organic matters in rhizospheric soils contributed to the increase of Cd sorption in soils. In Freundrich equation, k was a measurement of capacity of adsorption, representing the proportional to the equilibrium constant of ions sorption, and a is the parameter estimating the adsorption force, which showed a negative influence on amount of absorbed Cd. Table 3 illustrated the order of a: NR>R5≈R12 and the order of k: R12> R5>NR.

Table 3 Non-linear fitting parameters of sorption models of Cd adsorption in various rhizospheric soils

Treatments	Langmuir model			Freundrich model			Temkin model		
	X_m	a	R^2	k	a	R^2	k	a	R^2
NR	811.04	0.15	0.98	136.22	1.91	0.99	97.04	215.11	0.90
R5	948.06	0.15	0.95	153.97	1.81	0.98	116.92	245.68	0.92
R12	958.57	0.18	0.94	173.09	1.85	0.97	124.03	269.94	0.93

NR is non-rhizospheric soil. R5 is rhizospheric soil treated with five maize plants. R12 is rhizospheric soil treated with twelve maize plants.

Absorbed Cd by electric sorption (non-specific sorption) can be desorbed by Na^+, K^+ and Ca^{2+} from soil solid phase and enter into solution again. The more the amount of Cd desorbed by $NaNO_3$ is, the more availability of Cd to plant in soil. With the enhancement of soil adsorption, desorbed Cd increased significantly (Fig. 3). Apparently, the amount of desorbed Cd in non-rhizospheric soil (NR) was higher than that in rhizospheric soil (R5, R12), especially at the range of the higher Cd adsorption. Combining the results of adsorption, a preliminary conclusion can be given that under the rhizospheric effects of maize plant, Cd was easier to be adsorbed by soil, and more difficult to be desorbed.

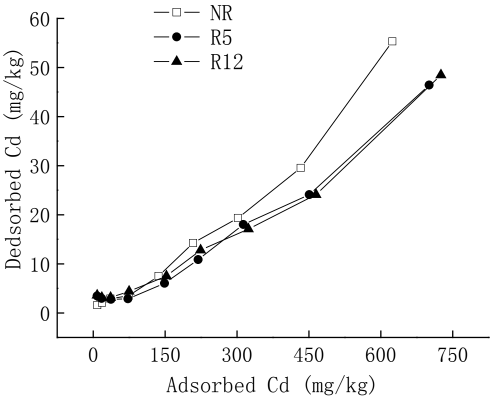

Fig. 3 Desorption curves of Cd under different rhizospheric effects.
NR is non-rhizospheric soil. R5 is rhizospheric soil treated with five maize plants. R12 is rhizospheric soil treated with twelve maize plants.

3.3 Influence of pH on Cd sorption

When the pH in equilibrium solutions increased, Cd sorption by various soils increased significantly (Fig. 4). The amounts of absorbed Cd by NR, R5 and R12 were elevated by 12.5%, 12.3% and 15.9% in the pH range from 4.5 to 8.1, respectively, which was accordance to many previous studies [7, 16]. The higher pH in solutions could accelerate the process of specific sorption of Cd in soil colloid particle surfaces, which is accompanied by release of H^+. The pH range, according to the Cd adsorption amount, can be divided into two stages, namely, rapidly increasing stage (pH<5.6) and slowly increasing stage (pH>5.6). But it was worth noting that unlike the isotherm sorption, no significant difference was observed among three soil samples under the same pH condition. This phenomenon further demonstrated that the more amounts of Cd absorbed by rhizospheric soil were mainly caused by the higher pH in rhizospheric environment.

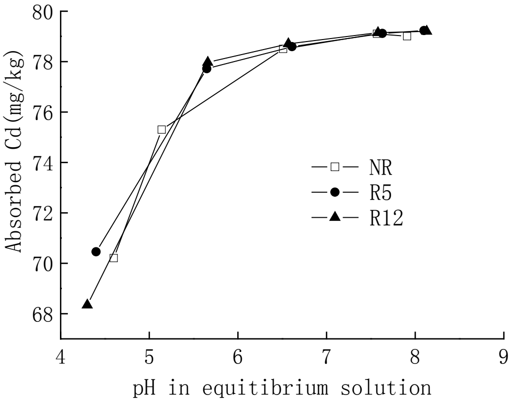

Fig. 4 Influence of pH on Cd adsorption by soil under rhizospheric effect.
NR is non-rhizospheric soil. R5 is rhizospheric soil treated with five maize plants. R12 is rhizospheric soil treated with twelve maize plants.

CONCLUSION

Rhizospheric effects induced by maize plants resulted in the enhancement of DOC and pH and reduction of Eh in rhizospheric soil. The amount of adsorbed Cd in rhizospheric soil was higher than that in non-rhizospheric soil. Freundrich model was the optimal equation to fit the sorption data of three soil samples. The fitting results showed that the maximum and capacity of Cd adsorption was elevated greatly in rhizospheric soil. The increasing pH promoted greatly the amount of adsorbed Cd in soils. However, no significant variation was presented between in rhizospheric soil and in non-rhizospheric soil at the same pH in solutions. It indicated that the change of pH may be the primary factor resulting in the enhancement of Cd adsorption in rhizosphere.

Acknowledgments

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