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Adsorption of Cd(II) by rhizosphere and non-rhizosphere soil originating from mulberry field under laboratory condition

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ABSTRACT
In this study, the adsorption behavior of Cd ions by rhizosphere soil (RS) and non-rhizosphere soil (NS) originated from mulberry field was investigated. The Langmuir, Freundlich and the Dubinin–Radushkevich (D-R) equations were used to evaluate the type and efficiency of Cd adsorption. The RS was characterized by lower pH but the higher content of soil organic matter and cation exchange capacity (CEC) as compared to NS. Also, the maximum adsorption of Cd$^{2+}$ for RS (3.87 mg/g) was slightly bigger than that for NS (3.36 mg/g). In Freundlich isotherm, the $K_f$ of the adsorption of Cd$^{2+}$ to surface of the RS components was higher than that of the NS, indicating stronger attraction between Cd$^{2+}$ and components of the RS. According to the D-R model, the adsorption of Cd$^{2+}$ by both soils was dominated by ion exchange phenomena. These results indicated that mulberry roots modified physical and chemical properties of the RS under field conditions, which also affected the Cd sorption efficiency by soil components during laboratory experiments. Current knowledge of the Cd$^{2+}$ sorption processes in the rhizosphere of mulberry may be important if these trees are planted for use in phytoremediation of Cd contaminated soils.

KEYWORDS
adsorption; heavy metal; cadmium; rhizosphere soil; mulberry

Introduction
Cadmium (Cd) is a non-essential element of the human body and is a highly toxic environmental pollutant which can be discharged into the environment mainly from the metallurgy, ceramics, electroplating industry and chemical industry (Abdus-Salam and Bello 2015). Cd could be easily absorbed and enriched by plants and further accumulated in the human body through the food chain. Long term intake of Cd polluted foods could cause a number of acute and chronic poisoning symptoms that bring about serious harm to kidneys, lungs, bones and the liver (Bradl 2004). Heavy metals contaminated soil has turned into a worldwide environmental issue, leading to a concern in innovating effective and reasonable treatment methods (Zhong et al. 2015). Phytoremediation, that takes advantage of plants to extract and detoxicate heavy metals, assimilate and degrade organic pollutants, is a prospective technology (Jiang et al. 2017). It is a green and relatively novel technique and is considered as a cost-efficient, eco-friendly technology with better public recognition (Ali et al. 2013).

Although hyperaccumulators in the phytoremediation of heavy metal polluted soil would have shown a dominant position, the practical use of them is blocked as a result of the shallow roots, slow growth, and less biomass (Wang et al. 2008). So the total amount of heavy metals absorbed and enriched by hyperaccumulator is not too much and the remediation efficiency is not too high (Jiang et al. 2017). For this reason a lot of researchers have pointed out that the utilization of some trees could be an alternative method for the extraction or detoxification of heavy metals from polluted soils (Peng et al. 2012; Jiang et al. 2017). Mulberry trees also have the potential to remediate heavy metals contaminated soils (Zhou et al. 2015; Jiang et al. 2017). Mulberry is a perennial woody tree with the features of deep root systems, rapid growth, and high biomass. Though the concentration of heavy metal in mulberry is lower than that of the hyper accumulator, the total amount of heavy metal extraction is impressive due to the large number of biomass (Jiang et al. 2017). Jiang et al. (2017) have reviewed, what it is also very important, that the leaves originated from the mulberry trees cultivated in heavy metal contaminated areas can be used to feed silkworms, because their growth and development, as well as the production and quality of silkworms cocoons were insignificantly lower quality in compare to those obtained from silkworms fed with unpolluted leaves. Developing sericulture may be a safe, economical, eco-efficient utilization of heavy metals contaminated areas (Zhou et al. 2015; Jiang et al. 2017).

However, the utilization of mulberry in phytoextraction is hindered by insufficient knowledge of numerous fundamental rhizosphere processes. Particularly the mechanisms of uptake of cadmium from soils are not clear and difficult to determine, because the rhizosphere is the zone where numerous interactive processes occur, including growth of roots and microorganisms, respiration, water and nutrient uptake, and rhizodeposition (Xin et al. 2015). Plants can change the rhizosphere environment to promote absorption of nutrient elements such...
as N, P, Zn and Fe. The basic mechanisms are acidification, a decrease of redox potential, and excretion of root exudates (Tu et al. 2004; Zeng et al. 2017). Li et al. (2011) have reported that water-soluble concentration of heavy metals in the rhizosphere of plants was greatly reduced. Furthermore, this decrease in water-soluble of metals commonly held only a small proportion of the total heavy metal accumulated by the plants, showing that the heavy metals are also released from less available pools (Li et al. 2011). Xin et al. (2015) explored the roles of low molecular weight organic acids secreted by roots in the uptake, translocation, and accumulation of Cd in a low-Cd and high-Cd hot pepper cultivars. Their results showed that despite the insignificant difference in amounts of exchangeable Cd between the rhizosphere soils of these two cultivars and the roots of the low-Cd cultivar excreted significantly less tartaric acid and more oxalic and acetic acids than plants belonging to the high-Cd cultivar. Therefore, some kinds of low molecular weight organic acids efflux from hot pepper roots played an important role in the difference of Cd accumulation between low- and high-Cd cultivars. Also, the experiment conducted by Hu et al. (Hu et al. 2011) very clear demonstrated effect of rhizosphere of two rice cultivars (Zhenong 54 and Sixizhan) on Cd distribution between three factions: exchangeable Cd, Fe/Mn oxide-bound Cd and organic matter-bound Cd. Authors indicated the significant differences in speciation of Cd, especially within fractions of exchangeable and oxide-bound Cd, depending on the rice cultivars, stage of plants growth and distance between soil and root. The lowest amount of exchangeable Cd in soil planted with Zhenong54 appeared in the near-rhizosphere area with little difference between tillering stage and ripening stage, while in soil planted with Sixizhan cultivar lowest exchangeable Cd concentration was in the rhizosphere. Comparing both cultivars only slight changes in the Fe/Mn oxide-bound fraction of Cd at the grain ripening stage was found, while the control treatments without plants was characterized by a significant increase amount of Cd in Fe/Mn oxide-bound fraction at the same time. These observations indicated a significant effect of the rhizosphere on mobilization of Cd from a less (Fe/Mn oxide-bound fraction of Cd) to more bioavailable forms (exchangeable Cd).

The risk of leaching or uptake of Cd by plants depends on the concentration of Cd in soil solution, which in turn depends on the sorption-desorption equilibrium that governs the partition of Cd between soil solution and soil solids, soil colloids especially (Covelo et al. 2007; Al-Oud et al. 2014). The rhizosphere processes are known to have a strong effect on the physical and chemical properties of soils and ultimately on the adsorption and phytovailability of Cd (Motaghan and Hosenipur 2015). The results of the pot experiment conducted by Li et al. (2013) indicated that the rhizosphere soil solution pH was significantly decreased due to enhanced exudation of dissolved organic matter (DOM) and Cd-DOM complexes were the dominant form of Cd in the soil solution when hyperaccumulating ecotype Sedum alfredii were planted. The formation of soluble Cd-DOM complexes in the rhizosphere of hyperaccumulating ecotype of Sedum alfredii could increase Cd mobility. However, rhizosphere processes that dominate heavy metal accumulation have not yet been completely illuminated. Also, the effect of mulberry tree roots on the mobilization of Cd in the rhizosphere is still indecisive. In this study, the adsorption of Cd ions by rhizosphere soil (RS) and non-rhizosphere soil (NS) originated from mulberry field were investigated. The Langmuir, Freundlich and the Dubinin–Radushkevich (D–R) equations were used to evaluate the type and efficiency of Cd adsorption. Our results explicate the possible mechanism of the rhizosphere effect of mulberry root on Cd mobilization in soil, and provide new insights into the use of mulberry for utilization of the Cd polluted soils.

**Materials and methods**

**Preparation of adsorbent and adsorbate**

The adsorbent used in this study, rhizosphere (RS) and non-rhizosphere soil (NS) of mulberry, were sampled from the mulberry garden (28°11'34"N, 113°4’59"E) in the Sericultural Research Institute of Hunan Province, China. RS and NS of mulberry were sampled by shaking root method (Chen et al. 2015). Soil samples were air-dried, ground to pass through a 2-mm sieve, and kept in plastic bags until use. The basic physical and chemical properties of the soil were measured by the method proposed by Lu (1999).

Flasks (1 L) were immersed in 1 mol/ L HCl solution for 24 h and then rinsed with deionized water (DW) three times. Cd (II) stock solution (1g/L) was prepared by dissolving cadmium chloride (analytical reagent grade) into deionized water.

**Adsorption experiment and adsorption isotherms**

Cd sorption by RS or NS was determined by a batch equilibrium experiment. One g soil sample was weighed and put into 50 mL-plastic centrifuge tubes. Then 25 mL solution, containing 0.5, 10, 25, 50, 100, 150, 200, 300 mg/L of Cd, was added to centrifuge tubes, respectively. The ionic strength of the soil solution was adjusted with 2.0, 2.0, 1.9, 1.8, 1.7, 1.4, 1.0, 0.7, 0.0 mL NaNO₃ (0.1 M) respectively and ignored the volume change of the solution. The centrifuge tubes with soil suspension were shaken for 24 h at 25 ± 1°C in a shaken bath (Yan et al. 2009), and then the soil samples were centrifuged at 5000 × g for 10 min. The Cd concentration in the supernatant was determined by atomic absorption spectroscopy (Agilent 3510, USA). The content of Cd adsorbed by the soils was computed from the differences between the initial and final concentrations of Cd in the equilibrium solution. Control tests and parallel tests (n = 3) were also conducted and the data results were averaged.

Langmuir, Freundlich and D–R equations were applied for depicting the adsorption characteristics. The Langmuir adsorption equation is:

$$q_e = q_{max} \frac{bC_e}{1 + bC_e}$$  \hspace{1cm} (1)

Or

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b \times q_{max}}$$  \hspace{1cm} (2)

where $C_e$ (mg/L) is the equilibrium solute concentration in the bulk metal suspension, $q_e$ (mg/g) is equilibrium adsorption capacity of heavy metal on the soil, $q_{max}$ (mg/g) is the
maximum adsorption quantity of the adsorbent, and \( b \) (L/mg) is the Langmuir adsorption constant. Another parameter \( R_L \), a dimensionless constant separation parameter, is provided by the following equation (Wu et al. 2014):

\[
R_L = \frac{1}{1 + bC_0}
\]  

(3)

where \( C_0 \) is the highest initial concentration of \( \text{Cd}^{2+} \) (mg/L). The Freundlich adsorption equation is

\[
q_e = K_f C_e^{1/n}
\]  

(4)

Or

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]  

(5)

where \( K_f \) [(mg g\(^{-1}\)) (L mg\(^{-1}\))\(^{1/n}\)] and \( 1/n \) are constants (Liu et al. 2012; Zhong et al. 2015). \( q_e \) was obtained using the equation:

\[
q_e = \frac{C_0 - C_e}{W}
\]  

(6)

where \( W \) (g/mL) is the amount of the adsorbents in per unit volume of aqueous solution.

The D-R adsorption equation is:

\[
\ln q_{e1} = \ln q_{\text{max}} - \beta e^2
\]  

(7)

where \( \beta \) (mol\(^2\)/kJ\(^2\)) is the activity coefficient related to the average adsorption energy \( (E, \text{kJ/mol}) \). \( e \) is the Polanyi potential, which could be given as:

\[
e = RT \ln \left( 1 + \frac{1}{C_e} \right)
\]  

(8)

where \( R \) and \( T \) are the ideal gas constant (8.314 J/(mol. K)) and absolute temperature in Kelvin (K), respectively. The relation between the mean adsorption energy and the activity coefficient is as follow:

\[
E = \frac{1}{\sqrt{2\beta}}
\]  

(9)

The value of \( E \) could be utilized to evaluate the mechanism of the adsorption reaction. If \( E \) is in the range of 8~16 kJ/mol, this indicates that the adsorption reaction is controlled by ion exchange or chemisorption. However, physical forces may affect the adsorption at the condition of \( E < 8 \) kJ/mol (Saeed, 2003; Lu et al. 2015).

### Results

Characterization of the sorbent

The basic physicochemical properties of the soil are showed in Table 1. In this study, the RS solution pH was reduced by 0.59 units, compared to the NS solution. The content of organic matter and soil cation exchange capacity (CEC) of RS were both higher than those of the NS. The RS particle size below 0.002 mm was 26.59 percent, more than that of the NS (24.14%).

### Adsorption isotherms

Langmuir, Freundlich and D-R equations were applied for depicting the adsorption characteristics. The comparison of parameters in the three equations obtained at the two different soils was to offer data concerning the role of RS or NS in Cd adsorption.

Equation (2), (5) and (7) were employed to simulate the experimental data. The adsorption isotherms were displayed in Fig. 1. The retrieved adsorption equation parameters were showed in Table 2. The adsorption of \( \text{Cd}^{2+} \) on RS or NS fit Freundlich, D-R and Langmuir equation well, as indicated by the higher determination coefficients \( R^2 \) (Table 2). In the Freundlich equation, the \( K_f \) of adsorption of \( \text{Cd}^{2+} \) to RS and NS surface were close, 0.69 [(mg g\(^{-1}\)) (L mg\(^{-1}\))\(^{1/n}\)] and 0.65 [(mg g\(^{-1}\)) (L mg\(^{-1}\))\(^{1/n}\)], respectively (Table 2). The \( E \) values for RS and NS obtained from the D-R equation were 11.79 and 11.47 kJ/mol, respectively (Table 2).

### Discussion

The pH value has been considered as one of the most significant factors by altering the surface charge of the adsorbent and also the distribution of heavy metal species in solution phase (Park et al. 2011; Huang et al. 2015). The main reasons for varieties of the rhizospheric pH include the activity of the proton pump, absorption imbalance of nutrients and metallic cations, production of respiratory CO\(_2\) and the release of organic acids as well as protons by plant roots (Javed et al. 2017). Generally, the changes of pH in the rhizosphere are controlled by the inorganic cation–anion balance in the plant and the correlative release of H\(^+\) or OH\(^-\) from the roots (Li et al. 2013). The RS solution pH was reduced by 0.59 units in this paper. This was consistent with the result of the reference (Li et al. 2011), which reported that the rhizosphere soil reduced by 0.5~0.6 units when the hyperaccumulating ecotype Sedum alfredii was planted in soil. The reduction of pH in RS solution was possibly owing to the increased excretion of root exudates, which was in line with the enhanced organic matter derived from root exudation in the RS (Table 1). The functional groups, such as

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>Organic matter (%)</th>
<th>CEC (cmol (+)/kg)</th>
<th>Particle size (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2~0.02 mm</td>
</tr>
<tr>
<td>RS</td>
<td>6.82</td>
<td>1.25</td>
<td>2.93</td>
<td>34.15</td>
</tr>
<tr>
<td>NS</td>
<td>7.41</td>
<td>1.02</td>
<td>2.13</td>
<td>35.68</td>
</tr>
</tbody>
</table>
when pH increases, H$^+$ separates from the functional groups such as carboxyl, phenolic, hydroxyl and carbonyl groups, the soil surface is negatively charged and as a result metal cations could be partly removed from the soil solution, thereby increasing the affinity for metal cations (Yang et al. 2006; Park et al. 2011). That is because the adsorption of heavy metals is also highly dependent upon soil components and properties including redox potential, silicate clays and cation/anion exchange capacity and so on but not a single factor account for their adsorption on soil (Park et al. 2011).

Soil organic matter (SOM) is another dominant factor affecting the availability of metals in soil (Huang et al. 2017). SOM refers to all organic matter that exists in the soil. It mainly includes various animal and plant residues, microorganisms and their decomposition and synthesis of various organic substances. SOM contains many functional groups, which can be adsorbed, complexed, reduced or oxidized with heavy metal ions, thereby affecting the phytoavailability of heavy metal ions (Fan et al. 2015). However, the SOM increases (Han et al. 2006; McCauley et al. 2009) or reduces (Lu et al. 2014; Mani et al. 2015) the bioavailability of Cd were determined by the forms of SOM. Dissolved organic matter can form soluble complexes with Cd, while particulate organic matter may enhance the soil adsorption of Cd to reduce the availability of Cd (Huang et al. 2017).

Soil cation exchange capacity (CEC) is the total amount of various cations that can be adsorbed by soil colloids, which is an important basis for evaluating soil fertility, improving soil fertility and reasonable fertilization. The CEC of RS was higher than that of the NS, indicating that the RS colloids have more negative charge and can adsorb more heavy metals by electrostatic reactions. Generally, fine grained soils have more retention potential for heavy metal than that of coarse grained soils because that the fine soils contain many active surface sites such as clay minerals, iron and manganese oxyhydroxides, and humic acids (Bradl, 2004).

The Langmuir model is based upon the following assumptions, these are: (i) adsorbate forms a mono layer on absorbent surfaces which contains a limited number of identified sorption sites; (ii) adsorbate and adsorption site keep a one-to-one regulation of interaction; (iii) dimension of the site-to-site distance is larger than that of the adsorbate and the interactions between the adsorbed adsorbate is negligible (Saha et al. 2005; Crini and Badot 2008). According to the Langmuir isotherm, it could be found that the monolayer saturation adsorption capacity ($q_{\text{max}}$) of RS was bigger than that of the NS, indicating that RS has more adsorption sites. These results are consistent with those shown in Table 1. The $R_L$ values indicate that the isotherm is unfavorable ($R_L > 1$), favorable ($R_L < 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$) (Wu et al. 2014). In the present study, $R_L$ values of RS and NS were 0.04 and 0.03, respectively, which indicates that the adsorption is a favorable process.

![Figure 1. Adsorption isotherms of Cd$^{2+}$ on RS and NS (a, Langmuir; b, Freundlich; c, D-R).](image-url)

| Table 2. Regressed constants for Cd$^{2+}$ on soils. |
|-----------------|-----------------|-----------------|-----------------|
| Langmuir | Freundlich | D-R | |
| $q_{\text{max}}$ | $b$ | $R_L$ | $R^2$ | $K_1$ | $1/n$ | $R^2$ | $\beta$ | $E$ | $q_{\text{max}}$ | $R^2$ |
| RS | 5.87 | 0.08 | 0.04 | 0.98 | 0.69 | 0.49 | 0.99 | $3.60 \times 10^{-3}$ | 11.79 | $1.37 \times 10^{-4}$ | 0.99 |
| NS | 5.36 | 0.10 | 0.03 | 0.98 | 0.65 | 0.44 | 0.96 | $3.80 \times 10^{-3}$ | 11.47 | $1.55 \times 10^{-4}$ | 0.97 |

Carboxyl, amino, and hydroxyl groups in organic matters, provide more adsorption sites, play important roles in increasing the adsorption of heavy metals (Liu et al. 2011). However,
The Freundlich equation is a purely empirical equation which is based upon the hypothesis of a heterogeneous adsorbent surface and it is not confined to the monolayer adsorption (Zhong et al. 2015). The magnitude of $K_F$ is determined by both the intensity of adsorption interaction and the relative adsorption quantity of the adsorbent for the associated adsorbate. $1/n$ is related to the adsorption intensity. The adsorption isotherm can be classified into S-, L-, and C-type according to the values of $1/n$. When $1/n < 1$, the adsorption isotherm is the L-type, indicating a relatively high affinity between the adsorbate and the adsorbent. When $1/n = 1$, the adsorption isotherm is C-type (linear), showing moderate adsorption force and the adsorption sites are uniform. When $1/n > 1$, the adsorption isotherm is S-type, suggesting the adsorption process is physical adsorption and the interactions between adsorbate and adsorbent is stronger than that of adsorbate and adsorbent (Yuan et al. 2007; Zhong et al. 2015).

The $K_F$ for adsorption of Cd$^{2+}$ to RS surface was a little higher than that of the NS, indicating strong attraction between Cd$^{2+}$ and RS. The more the adsorption capacity of Cd (II) on the RS, the less Cd (II) existed in soil solution, less Cd (II) absorbed by mulberry root. If Cd binds preferentially to carbonates, indicating greater mobility and availability to plants. Metal associations with particulate organic fractions are less dangerous for the environment and plants than exchangeable and carbonate fractions because these fractions are less extractable and less available, but when the environment becomes increasingly reducing or oxidizing, they can be mobilized (Mouni et al. 2017). So the various kinds of SOM from mulberry roots should be separated and its effect on the phytoavailability of Cd to mulberry tree should be studied further.

Furthermore, faced with heavy metal stress, the plant would secrete some organic substances for complexion or precipitation of heavy metal ions, such as sugars, amino acids, and carboxylic acids (Motaghian and Hosseinpur 2015). This could be a plant’s self-protection. Similarly, Javed et al. (2017) investigated the root exudation of the maize cultivar 3062 and 31P41 under Cd stress (0, 10, 20, 30, 40, 50 μmol/kg soil). These results indicated that the concentration of different organic acids (citric acid, malic acid, formic acid, acetic acid, oxalic acid and glutamic acid) was significantly increased in the root exudates of cultivar 3062 with applied Cd levels. But this effect was diminished in cultivar 31P41 at high Cd levels. As shown in Table 2, for both NS and RS, $1/n$ was lower than 1, suggesting a strong adsorption interaction between Cd$^{2+}$ and soils under experimental conditions (Huang and Liu 2013; Zhong et al. 2015).

The D-R equation represents the adsorption regularities at a homogeneous or constant adsorption potential (Lu et al. 2015). The value of sorption energy ($E$) in the range of 9–16 kJ/mol forecasts the chemisorption (Saeed, 2003). In this study, the $E$ values of RS and NS obtained from the D-R equation were 11.79 and 11.47 kJ/mol, respectively. Both of them were in the sorption energy range of chemical ion exchange reaction (Table 2), indicating that Cd(II) sorption to soils are attributed to chemical sorption rather than physical sorption (Saeed, 2003; Zhang et al. 2011). The parameters from the Langmuir, Freundlich and D-R equations manifest that the sorption of Cd(II) on both RS and NS is a favorable and controlled by ion exchange process.

Conclusions

The interaction between the roots of mulberry and soil in the zone closest to the roots (rhizosphere), modified the physico-chemical properties of rhizosphere soil (RS) in compare to non-rhizosphere soil (NS) in the field conditions. The RS was characterized by lower pH but the higher content of clays and soil organic matter as well as higher cation exchange capacity as compared to NS, and as a result of these differences RS had more adsorption sites for Cd(II) than NS. According to the applied Freundlich, D-R and Langmuir equations, the adsorption of Cd(II) by RS and NS under laboratory conditions was controlled by ion exchange processes (non-specific adsorption). Cd immobilization by non-specific adsorption on the surface of soil component in the rhizosphere of mulberry trees made it possible for safe utilizing Cd contaminated soils.

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References


