



Investigation of the potential mobility of Pb, Cd and Cr(VI) from moderately contaminated farmland soil to groundwater in Northeast, China

Deming Dong*, Xingmin Zhao, Xiuyi Hua, Jinfu Liu, Ming Gao

College of Environment and Resources, Jilin University, Changchun 130012, China

ARTICLE INFO

Article history:

Received 10 August 2007

Received in revised form 27 March 2008

Accepted 8 June 2008

Available online 19 June 2008

Keywords:

Pb

Cd

Cr(VI)

Adsorption/desorption

Mobility

Soil

Groundwater

ABSTRACT

The adsorption/desorption of Pb, Cd and Cr(VI) on moderately contaminated farmland soils in Northeast China and the effect of pH value on adsorption/desorption were investigated. Soil column leaching experiment was also carried out to further understand the mobility of the three metals in aeration zone of soil. Both Langmuir and Freundlich model gave good fits to the adsorption data of Pb and Cd, while the adsorption data of Cr(VI) followed linear adsorption isotherm. The adsorption/desorption of Pb, Cd and Cr(VI) obtained equilibrium in a few hours. Adsorption amounts of the three metals decreased in the order: Pb > Cd >> Cr(VI). Desorption of the metals was insignificant at pH 5.0. Pb and Cd adsorption increased with pH, while Cr(VI) decreased. The effect of pH on desorption was contrary to that of adsorption. Leaching experiment showed that the mobility of these metals followed the order of Cr(VI) >> Cd > Pb, which was consistent with the adsorption/desorption study. The results suggest that once soil is polluted by wastewater containing Pb and Cd, Pb and Cd tend to accumulate in topsoil and move downward very slowly, while the mobility of Cr(VI) in soil/groundwater system is much high because only limited amount of Cr(VI) were adsorbed by soil.

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1. Introduction

Toxic heavy metals were widely used in industrial and agricultural production and brought great harms to plant and animal through food chain [1]. Many studies showed that adsorption was the most important process controlling existence of trace metals on solid phases, including soil [2–5]. In general, heavy metal adsorption and desorption process occurred simultaneously, and determined metal concentration in soil solution [6,7]. Improved understanding of adsorption and desorption characteristics may allow us to evaluate potential mobility of trace metal in soil. Although extensive researches were reported about metal adsorption on soil, however, compared with adsorption, only limited studies were focused quantitatively on the desorption of heavy metals to soil surface [8,9], and fewer studies combining heavy metal adsorption/desorption by batch experiments with heavy metal transport by column experiments were carried out to investigate heavy metal enrichment and migration ability in soil and the risk of heavy metal to groundwater.

Some studies found that metal adsorption/desorption process on soil was affected by many factors such as soil character, metal

ion character and pH of the soil system [10–14]. It was well accepted that pH was one of the most important geochemical parameters affecting adsorption and desorption of metal in soil [10,13].

Northeast China has been an important industrial base of the country for many years. With the development of industry, a great deal of pollutants from various anthropogenic sources such as industrial wastes, mining activity, wastewater irrigation and atmospheric deposition from burning fossil were discharged into the environment. In this article, adsorption/desorption characteristics of Pb, Cd and Cr(VI) by contaminated farmland soils from Northeast China were studied and the mobility of the three metals from the aeration zone of soil to groundwater was investigated through soil column leaching experiment. Here, Pb and Cd were chosen as representatives of trace metal cations because they were highly toxic common metals in soil and they had remarkably different hydrolysis constants, ionic radii and redox potentials [15]. Cr(VI) was selected as representative anion because that Cr(VI) was an oxyanion (e.g., CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$) and was more mobile in soil/groundwater system because of greater solubility and lesser adsorption by aquifer materials [16]. A research about trace toxic elements in farmland soils in Northeast China could provide valuable information for this region to estimate heavy metal pollution of soil/groundwater system. The main objectives of this study are: (1) to determine adsorption/desorption of Pb, Cd and Cr(VI) on moderately contaminated farmland soils in Northeast China, (2)

* Corresponding author. Tel.: +86 431 85166401; fax: +86 431 85166401.
E-mail address: dmdong@mail.jlu.edu.cn (D. Dong).

to provide an improved understanding and predictive capability of heavy metal transport in soil in an effort to better characterize the risk of contaminant migration and evaluate potential cleanup scenarios.

2. Materials and methods

2.1. Soil samples

Soil samples were collected from three sites in moderately contaminated farmland in Northeast China. Site A (42° 04.001'N, 123° 29.352'E) was about 60 m away from a landfill of chromium wastes. Site B (41° 38.05'N, 123° 4.35'E) was about 30 m away from a river seriously polluted by industrial wastewater and sewage. Site C (43° 53.503'N, 125° 05.839'E) was about 30 m away from another river mainly polluted by industrial wastewater.

Soils were thoroughly mixed and air-dried after removing gravel and plant residues. After 1 week, the soils were crushed using an agate mortar and then passed through a 100 mesh nylon sieve. Some basic physicochemical properties of these soils are shown in Table 1.

2.2. Adsorption experiment

Adsorption kinetics was carried out with two initial concentrations of each metal (0.818 and 4.090 mg/L for Pb, 0.902 and 9.130 mg/L for Cd, 1.037 and 11.032 mg/L for Cr(VI)) by dilution of 1000 mg/L Pb(NO₃)₂, Cd(NO₃)₂ and K₂Cr₂O₇ (all analytical grade reagent) stock solution with distilled-deionized water (dd H₂O). According to preliminary soil/solution adsorption experiment (not reported here), 0.4000 g soil was selected for Pb and Cd adsorption, and 50 g for Cr(VI) adsorption. Soil samples weighed precisely were transferred into beakers and submerged in 500 mL solution with different metal concentrations. The suspensions were stirred continuously with magnetic stirrers, maintaining pH value at 6.0 ± 0.1 by adding 1 mmol/L HNO₃ and 1 mmol/L NaOH. Adsorption time was determined for 2, 5, 15, 30 min, 1, 2, 4, 8, 16, 24 h, respectively. At the end of each adsorption period, the soil suspensions were centrifuged for 30 min at 5000 rpm, and the supernatants were collected for measurement of metal concentration. The concentration

of Pb or Cd was analyzed by a WYX-9004 Flame Atomic Adsorption Spectrometer (FAAS) (Shenyang Yitong Analytical Instrument Co., Ltd, China), and Cr(VI) was analyzed by 1, 5-diphenyl carbazide spectrophotometric method using a WFJ2-7200 Spectrophotometer (Unico (Shanghai) Instruments Co., Ltd., China).

The thermodynamics experiment of Pb, Cd and Cr(VI) adsorption was carried out for 24 h with initial metal concentrations ranging from 0.05 to 10 mg/L. This experiment followed the same procedure as described in adsorption kinetics.

For the effect of pH on adsorption, soil–liquid systems were previously adjusted to a series of pH values (ranging from 4.0 to 8.0). Initial concentrations for Pb, Cd and Cr(VI) were 5, 5, 10 mg/L, respectively. During adsorption process, pH was maintained at certain value by addition of HNO₃ and NaOH solution. After heavy metal adsorption, final pH values of soil solution were checked.

The adsorption amount of heavy metal was calculated as difference between metal concentration in original solution and that in equilibrium solution.

2.3. Desorption experiment

Soils previously adsorbed heavy metals for desorption kinetics. Complete adsorption of Pb or Cd by the soils was observed at the end of the incubation period and the concentrations of Pb and Cd in the incubated soils were 1020 and 1015 mg/kg, respectively, however, under the same conditions, the concentration of Cr(VI) in the incubated soils was only 51 mg/kg. 25 g polluted soils and 250 mL dd H₂O in beakers were stirred continuously maintaining pH value at 5.0 ± 0.1 (selected according to the possible pH value of acid precipitation in this area). At different time (2, 5, 10, 20, 30 min, 1, 2, 3, 4, 5, 6, 8, 11, 19.5, 24, 36, 48 h), a 10 mL aliquot was removed from suspensions, centrifuged, and the concentration of metal was measured.

The effect of pH (ranging from 2.0 to 8.0) on desorption was carried out for 48 h, which followed the same procedure as described in desorption kinetics.

In the experiments of adsorption and desorption, suspensions containing soil and dd H₂O without addition of heavy metal were used as the blank of this experiment, which underwent the same process as the experiment with heavy metal.

Table 1
Physical and chemical properties of the soils used in this experiment

Parameter	Soil A	Soil B	Soil C
Physical			
Sand (%) ^a	18 ± 1	16 ± 3	23 ± 2
Silt (%) ^a	58 ± 2	61 ± 6	51 ± 3
Clay (%) ^a	24 ± 0	23 ± 1	26 ± 2
Chemical			
pH	7.07	7.02	8.22
EC (μs/cm)	28	105	88
TOC (g/kg) ^b	14.30 ± 0.21	10.74 ± 0.32	9.83 ± 0.01
CEC (mmol/kg) ^b	157.06 ± 10.2	135.74 ± 2.10	157.99 ± 1.32
pHpzc	2.97	3.03	2.87
Total metal concentration (mg/kg)^b			
Lead (Pb)	60.71 ± 2.01	32.22 ± 1.08	24.27 ± 0.59
Cadmium (Cd)	0.43 ± 0.02	0.43 ± 0.05	1.24 ± 0.12
Chromium (Cr)	179.22 ± 2.09	30.16 ± 2.85	29.68 ± 3.41
Iron (Fe)	36840 ± 201	30960 ± 370	25050 ± 687
Manganese (Mn)	727.4 ± 12.3	457.9 ± 9.4	594.2 ± 21.2
Calcium (Ca)	2150 ± 124	2388 ± 650	3011 ± 301
Magnesium (Mg)	301 ± 12	241 ± 8	351 ± 14
Potassium (K)	586 ± 37	703 ± 13	632 ± 26

EC, electrical conductivity; TOC, total organic carbon; CEC, cation exchange capacity.

^a Mean ± S.E. (n = 2).

^b Mean ± S.D. (n = 5).

2.4. Soil column leaching experiment

Soil A was used for leaching experiment. A polyvinyl chloride (PVC) column, with an inner diameter of 18.5 cm and a length of 60 cm, was packed with air-dried soil on the basis of original depth layer and bulk density in the field. The small holes for sampling effluents were drilled at the depth of 20, 40, 60 cm, respectively. Before the leaching experiment, soils were saturated with dd H₂O at ionic strength of 0.01 mol/L CaCl₂ for 24 h. Three soil columns were leached with the solution containing 10 mg/L Cr(VI), 100 mg/L Pb and 100 mg/L Cd respectively (pH 6.0) at room temperature (18–20 °C) and the influent flow was controlled at 2.8 mL/min. At certain intervals, the effluents were collected for the measurement of heavy metal.

2.5. Statistical analysis

Three models were tested to describe the adsorption experimental results of Pb and Cd: the Langmuir model, the Freundlich and the Dubinin–Radushkevich model (D–R). The Langmuir isotherm has been successfully applied to study adsorption processes in solution and it has been used to explain the adsorption of solute onto many adsorbents [17]. The (D–R) isotherm is more general than the Langmuir isotherm since it does not assume a homogeneous surface or constant sorption potential. It was applied to distinguish between the physical and chemical adsorption of metal ions [18].

The Langmuir, Freundlich, and Dubinin–Radushkevich equations are expressed respectively by Eqs. (2)–(4):

$$\Gamma = \frac{\Gamma_{\max} K_L C_e}{(1 + K_L C_e)} \quad (1)$$

$$\Gamma = K_F C_e^{1/n} \quad (2)$$

$$\Gamma = \Gamma_{\max} \exp \left(-B \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \right) \quad (3)$$

where C_e is the equilibrium concentration of free metal ion in solution (mg/L), Γ is the adsorption amount of metal on soil (mg/kg), Γ_{\max} is the maximum adsorption amount of metal on soil (mg/kg), K_L is the Langmuir equilibrium coefficient (L/mg), K_F is the Freundlich adsorption coefficient (L/kg), n is a dimensionless parameter that varies between 0 and 1, depending on the character of adsorbent. B (mol²J⁻²) is a constant related to the adsorption energy, R (J mol⁻¹ K⁻¹) is the gas constant, and T (K) is the absolute temperature. The constant B gives the mean free energy E (kJ/mol) of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship [19]

$$E = \frac{1}{(2B)^{0.5}} \quad (4)$$

This parameter gives information about chemical or physical adsorption.

When partition of contaminant between solid and liquid phase is constant, adsorption of Cr(VI) is described by the following linear

adsorption isotherm:

$$\Gamma = K_L [M] \quad (5)$$

where K_L is distribution coefficient (L/mg).

Successful design of a column adsorption process requires prediction of breakthrough curve (BTC) for the effluents. The Thomas equation [20] of the form shown in Eq. (6) has been widely used for describing BTC.

$$\frac{C_e}{C_0} = \frac{1}{(1 + e^{(K_T(q_0 m - C_0 V))/Q})} \quad (6)$$

where C_e = element concentration in the effluent (mg/L); C_0 = initial concentration of element (mg/L); K_T = Thomas rate constant (mL/(mg·min)); q_0 = maximum amount of element that can be loaded (mg/g) under the specified condition; m = mass of the adsorbent (g); V = effluent volume (L); Q = flow rate (mL/min).

3. Results and discussion

3.1. The distribution of heavy metal in sampling sites

Different origin resulted in the difference of heavy metal content in soils. By comparing the data in Tables 1 and 2, it could be found that the content of Cr in soil A was greater than the first grade of environmental quality standard for soils, which was due to the presence of landfill of chromium wastes from site A approximately 60 m. The concentration of Cd in soil C was greater than the second grade of China soil standards (GB 15618-1995) because of long-term waste water irrigation in the past several decades. Although waste water irrigation was already prohibited, heavy metal pollution for majority of soils was serious, especially for Cd pollution. Site B was affected slightly by polluted river, therefore the content of heavy metal was relatively lesser than that of soil A and soil C.

3.2. The kinetics and thermodynamics of Pb, Cd and Cr(VI) adsorption on the soils

The data of adsorption kinetics for Pb, Cd, and Cr(VI) were fitted using Langmuir kinetics model (R^2 between 0.67 and 0.86) (Fig. 1). As shown in Fig. 1, at initial stage, the adsorption amounts of each metal increased remarkably with time, and during the first 30 min they were about 90% on average of total amounts of metal adsorbed within 24 h. Subsequently, there was a gradual increase of adsorption amounts until adsorption equilibrium was obtained at about 2 h for Pb and Cd, and 5 h for Cr(VI). Many similar studies about adsorption kinetics also indicated that metal adsorption could be divided into initial fast adsorption (from soil solution to external soil surface) and the following slow adsorption (by diffusion, into pores of inner soil surfaces) [21,22]. At initial stage, surface charge adsorption dominated, so adsorption reaction was fast. As adsorption time increased, intra-granular pore adsorption reaction occurred and was gradually dominant [22,23].

Adsorption data and adsorption isotherms of Pb, Cd and Cr(VI) on the three soils are shown in Fig. 2. Estimated Langmuir, Freundlich and D–R parameters for Pb and Cd adsorption and linear

Table 2

The value of environmental quality standard for soils (mg/kg)^a

Grade	First grade	Second grade			Third grade
pH value of soil	Natural background	<6.5	6.5–7.5	>7.5	>6.5
Pb	≤35	≤250	≤300	≤350	≤500
Cd	≤0.20	≤0.30	≤0.60	≤1.0	≤1.00
Cr (dry farmland)	≤90	≤150	≤200	≤250	≤300

^a Standard code: GB156198-1995.

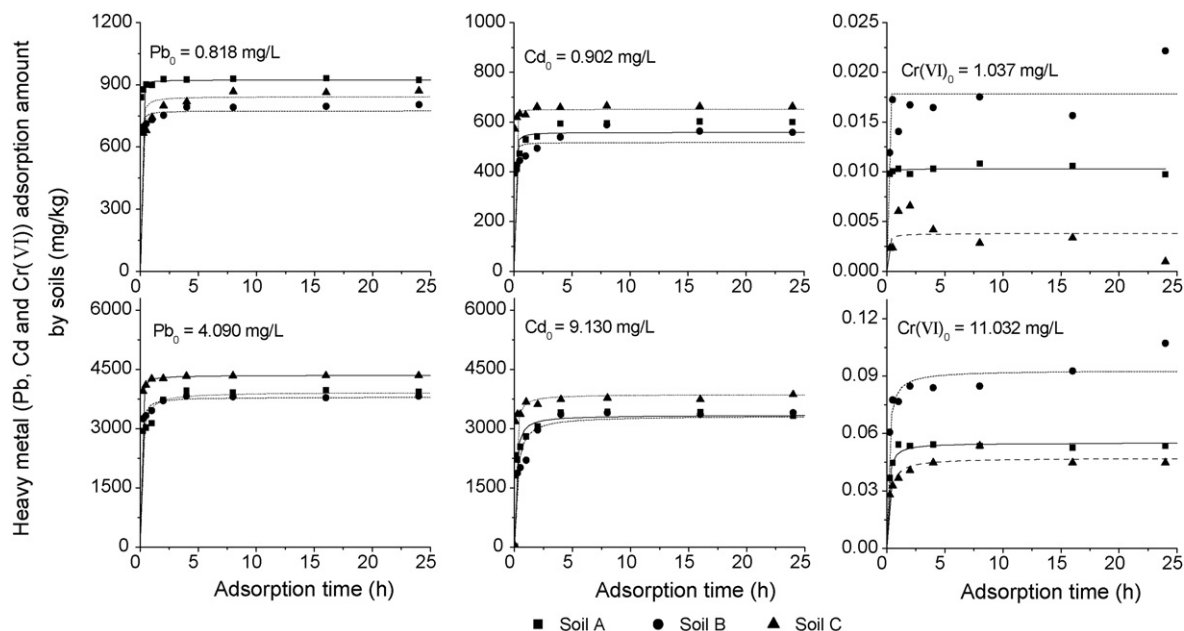


Fig. 1. Adsorption kinetics of Pb, Cd and Cr(VI) on the three soils at two initial metal concentrations.

parameters for Cr(VI) adsorption are listed in Table 3. Regression coefficient (R^2) showed that the data of Pb and Cd adsorption followed Langmuir, Freundlich and D–R adsorption isotherms and the data of Cr(VI) adsorption followed linear adsorption isotherm in the concentration range investigated here.

As shown in Fig. 2, for the three soils, the adsorption amounts of Pb were greater than that of Cd. It was also shown in Table 3 that the maximum adsorption amounts of Pb (5813–12,902 mg/kg) were greater than that of Cd (2872–4158 mg/kg). The difference between the adsorption amounts of Pb and Cd depended on ionic properties such as electronegativity, ionization potential, hydrolysis constants, ionic radius and redox potential [15]. Standard electrode potential and covalent radius were two of the principal characteristics, causing the variation of cation adsorption. The values of Γ_{\max} increased with the increase in values of the standard electrode potential of metal elements and decreased with the increase in values of covalent radius of metal elements. Standard electrode potential of lead and cadmium were recorded as 166.7 and 10.8, respectively and covalent radius of lead was less than that of cadmium [24], so the adsorption amounts of Pb by soil were greater than that of Cd. The mean free energy of adsorption E in the D–R equation gives information about adsorption mechanism as chemical adsorption or physical adsorption. The E value ranges from 1 to 8 kJ/mol for physical adsorption and ranges from 8 to 16 kJ/mol for chemical adsorption [25]. As shown in Table 3, the values of E calculated were 12.01, 11.56 and 10.19 kJ/mol for Pb adsorption, and 8.17, 8.56 and 8.81 kJ/mol for Cd adsorption. This meant that the type of adsorption of Pb or Cd onto the three soils was essentially chemical process. The similar results for the adsorption of Pb and Cd were reported by earlier workers [26].

The adsorption amounts of Pb or Cd were about 2–3 magnitude grade of that of Cr(VI). The similar law of Pb and other metals adsorption on soil was also found, for instance, Liu et al. [27] found that the adsorption amounts of metal on soil decreased in the order: Pb > Cd > Hg > Cr(VI), and Zhang et al. [28] found that the adsorption amounts on other followed the order: Pb > Cd > Cu > Zn. Different charge characteristic led to different adsorption ability between Pb (or Cd) and Cr(VI). Positively charged Pb and Cd were adsorbed by negative sites on the soil surface. Anionic Cr(VI) could be only

adsorbed by goethite, FeO(OH), aluminum oxides and other soil colloids with positively charged surface sites [29]. The pH_{Hpzc} of the three soils were 2.97, 3.03, 2.87 respectively, this indicated that soil surfaces were negatively charged, so, Pb²⁺ and Cd²⁺ were adsorbed greatly, which might result in reduced threat of Pb and Cd contamination to groundwater. However, only limited amounts of Cr(VI) were adsorbed by soil, so, compared with Pb and Cd, the mobility of Cr(VI) in soil/groundwater system was much high.

The adsorption amounts of Pb on soil A were little greater than that on soil C and less Pb was adsorbed by soil B. The adsorption amounts of Cd on the three soils followed the order: soil C > soil A > soil B. This result could be also found by comparing Γ_{\max} in the Langmuir equation and K_F in the Freundlich equation (Table 3). The adsorption amounts of Cr(VI) on the three soils were almost equivalent. Some factors, such as soil pH value, organic matter content, cation exchange capacity (CEC), and soil structure could affect adsorption ability of soil to heavy metal. pH value was an important parameter as described in Section 1. Organic matter in soil was also an important factor affecting metal adsorption: soil with high organic matter content often has great adsorption ability for metal. As CEC reflects the number of potential binding sites negatively charged, soil with high CEC can absorb more metal cations by electrostatic attraction. Organic matter content, CEC and pH value of soil B were all the smallest among the three soils, which could explain that the adsorption amounts of Pb or Cd on soil B were smallest among the three soils.

Pb and Cd could be adsorbed greatly by the three soils described as above, and adsorption achieved equilibrium so fast, therefore, Pb and Cd were immobilized in soil/groundwater. Soil adsorbed Cr(VI) fast too, but the adsorption amounts were limited, so Cr(VI) might have high mobility in soil/groundwater.

3.3. Desorption of Pb, Cd and Cr(VI) from the soils

After 48 h, the concentration of Cr(VI) in the desorption solution was lower than the detection limit of the analytical method. That could be a reason that the amount of Cr(VI) adsorbed on soils was so few that even fewer Cr(VI) desorbed from soils. For Pb and Cd, the concentration of heavy metal in equilibrium desorption

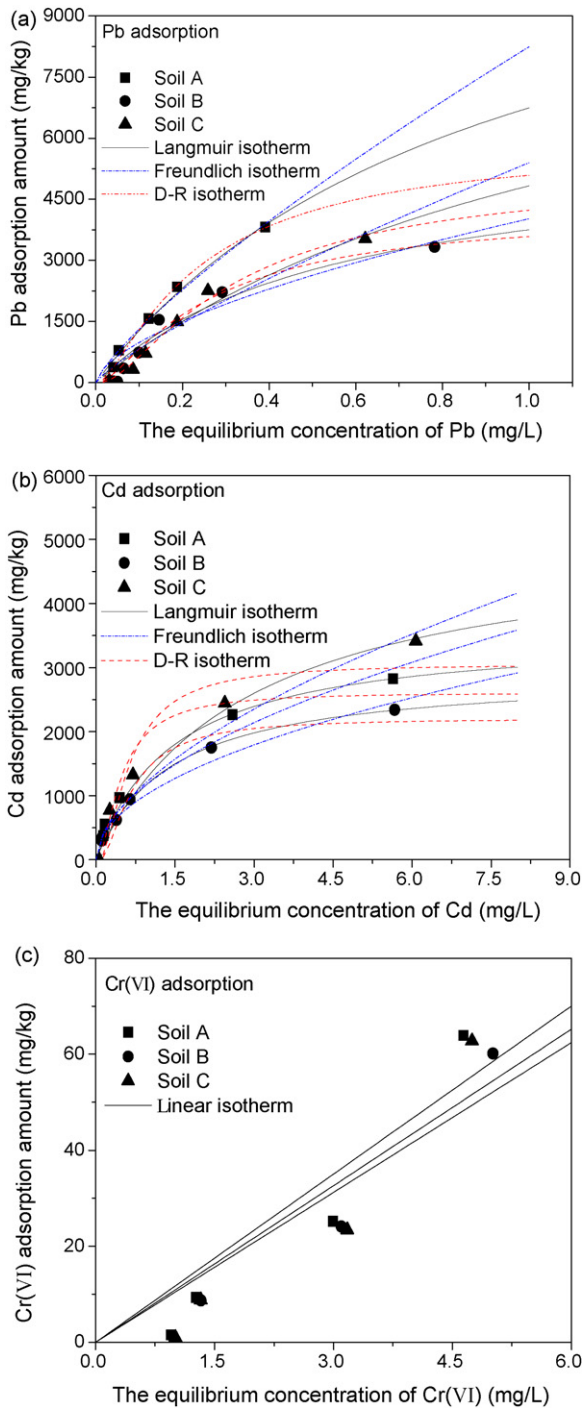


Fig. 2. Langmuir and Freundlich isotherms for Pb (a), Cd (b) adsorption and linear isotherms for Cr(VI) (c) adsorption on the three soils. Experimental data are reported as points.

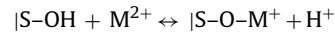
solution versus time by Langmuir kinetics model (R^2 between 0.70 and 0.95) are presented in Fig. 3. In each suspension sample, the whole concentration of metal released at different sampling time was increased with time. However, considering the mass of metal already in the solution, the mass of metal released with time was decreased, which could be explained by the decreased slope of desorption curve. For all these soils, Pb and Cd desorption achieved equilibrium at about 10 and 5 h, respectively. Compared with Pb, the desorption amounts of Cd during the first 1 h were remarkable, and about 70% of the total amounts of Cd were released during the entire

48 h. After desorption equilibrium, the amounts of Cd desorption were all about five times of that of Pb. According to this result, it could be concluded that compared with Cd, the three soils had great affinities for Pb. The percentages of Pb and Cd desorbed from the three soils were about 1–2% and 2–5% of the total metal amounts originally adsorbed, respectively. For three soils, the desorption amounts of Pb and Cd followed the order: soil B \geq soil C > soil A. Connecting the result of desorption with that of adsorption, it can be deduced that if soil is polluted by wastewater containing Pb and Cd, Pb and Cd can be adsorbed fast by topsoil and not easily desorbed, so move downward into groundwater very slowly.

3.4. The effect of pH on Pb, Cd and Cr(VI) adsorption/desorption

The effect of pH on metal adsorption on the three soils is shown in Fig. 4. With pH value increasing, the adsorption amounts of Pb and Cd were increased and the adsorption amounts of Cr(VI) were decreased. As shown in Fig. 5, the desorption amounts of Pb and Cd were decreased with pH value. At the same pH value, the desorption amounts of Cd were greater than that of Pb. In this study, Cr(VI) was not observed in the desorption solutions at all pH values.

Cationic metal adsorption/desorption on/from binding site of soil mineral surface was expressed by the following formula [30]:



In the formula, |S-O- represented adsorption site of mineral surface on soil (such as |Fe-O-, |Al-O-). This reaction formula was reversible, that is, high pH was advantageous for rightward reaction and low pH was advantageous for leftward reaction. At low pH value, metal cation faced competition with cation H^+ for available

Table 3

Langmuir, Freundlich, and Dubinin–Radushkevich parameters for adsorption of Pb and Cd and linear parameters for adsorption of Cr(VI) at pH 6.0

	Soil A	Soil B	Soil C
Pb adsorption			
Langmuir			
Γ_{max} (mg/kg)	12902 \pm 6022	5813 \pm 1549	10806 \pm 5910
K_L (L/mg)	0.23 \pm 0.14	0.38 \pm 0.18	0.17 \pm 0.12
R^2	0.98	0.94	0.95
Freundlich			
K_F (L/kg)	1239 \pm 81	777 \pm 118	794 \pm 101
n	0.86 \pm 0.10	0.67 \pm 0.13	0.84 \pm 0.14
R^2	0.97	0.90	0.94
Dubinin–Radushkevich			
Γ_{max} (mg/kg)	5763 \pm 368	4101 \pm 293	5029 \pm 285
E (kJ/mol)	12.01 \pm 1.01	11.56 \pm 1.26	10.19 \pm 0.91
R^2	0.96	0.93	0.90
Cd adsorption			
Langmuir			
Γ_{max} (mg/kg)	3920 \pm 114	2872 \pm 94	4158 \pm 263
K_L (L/mg)	0.11 \pm 0.01	0.08 \pm 0.01	0.08 \pm 0.01
R^2	0.91	0.99	0.99
Freundlich			
K_F (L/kg)	472 \pm 75	399 \pm 58	490 \pm 89
n	0.47 \pm 0.05	0.46 \pm 0.04	0.49 \pm 0.05
R^2	0.98	0.98	0.98
Dubinin–Radushkevich			
Γ_{max} (mg/kg)	2607 \pm 185	2203 \pm 168	3055 \pm 311
E (kJ/mol)	8.17 \pm 0.79	8.56 \pm 0.60	8.81 \pm 0.72
R^2	0.96	0.96	0.93
Cr(VI) adsorption			
Linear			
K_L (L/kg)	11.674	10.403	10.870
R^2	0.93	0.94	0.91

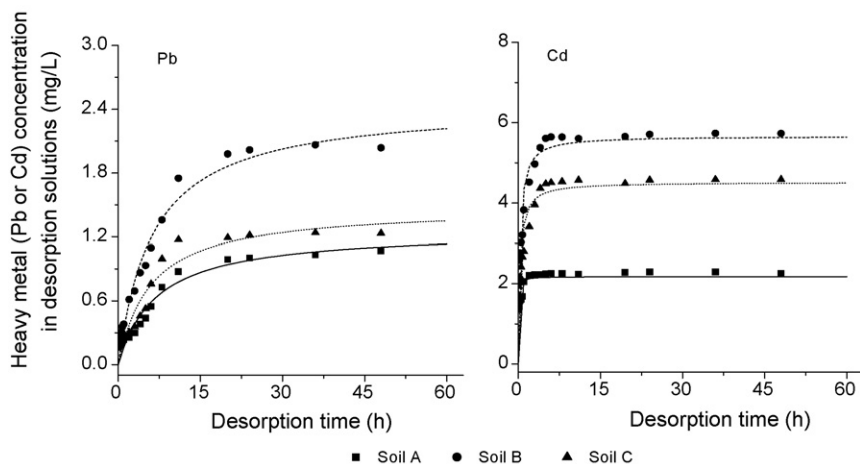


Fig. 3. Desorption kinetics of Pb and Cd from the three soils at pH 5.0.

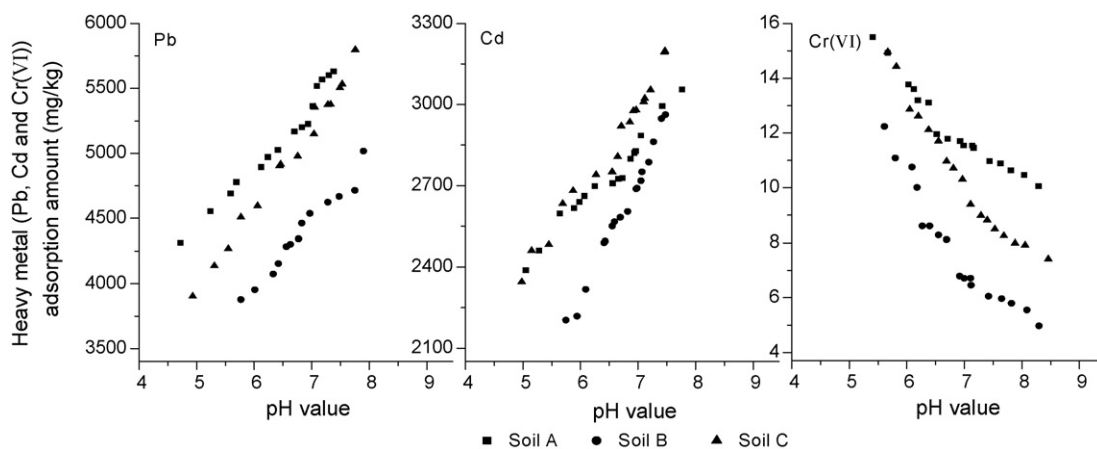


Fig. 4. Adsorption of Pb, Cd and Cr(VI) on the three soils as a function of pH.

permanent charged site. The exchange between H^+ and Cd^{2+} or Pb^{2+} was beneficial to Cd or Pb desorption and inhibited the adsorption reaction. Furthermore, because many adsorption sites on soils were pH value dependent (i.e., Fe and Mn oxides, carbonates, and clay minerals), when pH value was low, the oxides of Fe and Mn might

dissolve and released adsorbed metal ions into solution [29]. The adsorption amounts of Cr(VI) decreased with pH increasing due to the decrease of positive surface charge in soil. Some study also indicated that adsorption of Cr(VI) increased as pH decreased, no matter what sorbent [31].

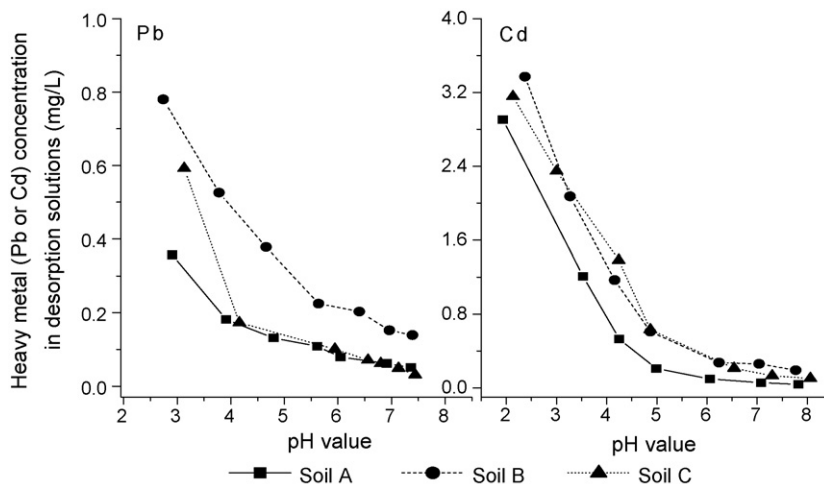


Fig. 5. Desorption of Pb and Cd from the three soils as a function of pH.

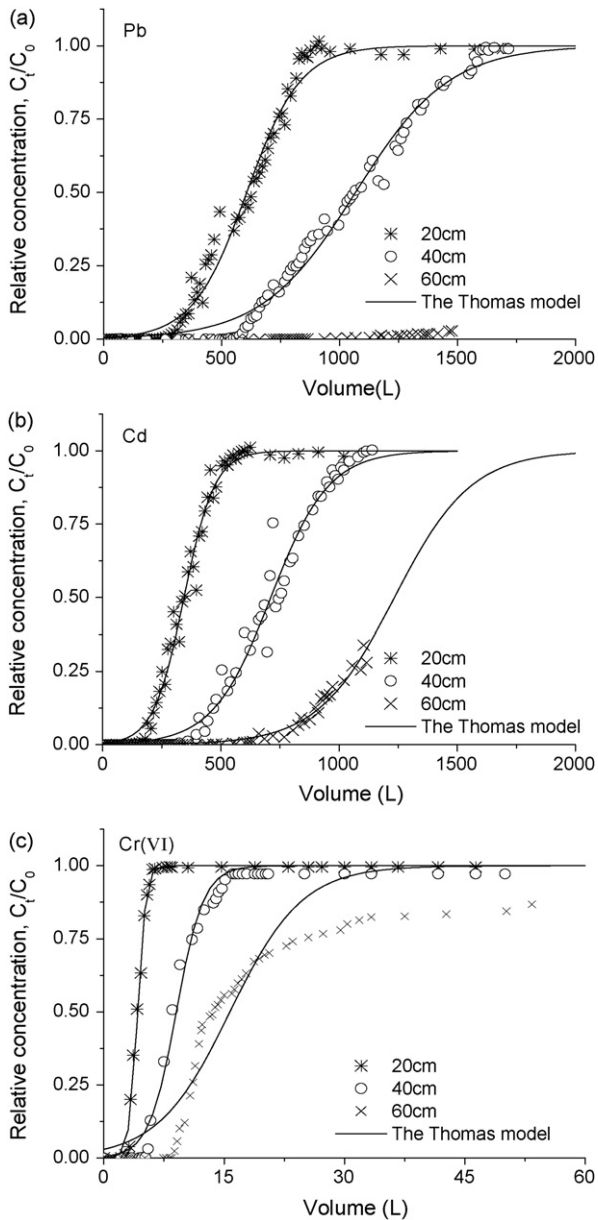


Fig. 6. Comparison of the experimental and predicted breakthrough curves obtained according to the Thomas model for Pb (a), Cd (b) and Cr(VI) (c).

3.5. The mobility of Pb, Cd and Cr(VI) in aeration zone of soil

Non-linear regression of the breakthrough data using Thomas equation are shown in Fig. 6, for Pb, Cd and Cr(VI), respectively.

Table 4
Parameters predicted from the Thomas model for Pb, Cd and Cr(VI) leaching experiment

Heavy metal	Depth of soil profile (cm)	C_0 (mg/L)	K_T (mL/(mg·min))	$q_{0,cal}$ (mg/g)	$q_{0,exp}$ (mg/g)	R^2
Pb	20	100	0.00024	12.126	10.475	0.986
	40	100	0.00014	10.675	10.359	0.988
	60	100	–	–	–	–
Cd	20	100	0.00043	6.875	5.467	0.988
	40	100	0.00023	7.107	5.367	0.984
	60	100	0.00017	8.225	4.965	0.973
Cr(VI)	20	10	0.537	0.0084	0.0112	0.992
	40	10	0.165	0.0090	0.0122	0.989
	60	10	0.062	0.0105	0.0100	0.892

Inspection of each of regressed lines indicated that they were all acceptable fits with R^2 ranging from 0.973 to 0.992 except Cr(VI) in effluent at the depth of 60 cm. During the experiment, saturation was not reached at 60 cm for Cr(VI) leaching, which might due to intense deoxidization in deeper soil profile. As shown in Fig. 6, much sharper breakthrough curves were obtained for Cr(VI) leaching because of its lesser adsorption capacity by soil. Breakpoint time for Cr(VI) appeared rapidly at 5, 30 and 60 h for the sampling depth of 20, 40, 60 cm respectively and maximum concentration in effluent was reached at 40, 96, 320 h, respectively. However, for Pb and Cd, the concentration in leachate increased more slowly and the breakpoint time appeared later (about several hundred to several thousand of hours) than that of Cr(VI). Comparatively, the mobility of Cd was higher than that of Pb. The values of K_T and q_0 are presented in Table 4. As the depth of soil profile increased, the values of K_T decreased and q_0 was almost constant for each metal. The predicted and experimental values of the soil capacity (q_0) obtained for three metals showed negligible difference. According to the value of K_T (presenting the rate of pollutants transportation in the soil profile), the rates of the three metals transportation in aeration zone of soil followed the order Cr(VI) \gg Cd > Pb, which was consistent with the result concluded from static adsorption/desorption.

3.6. The prediction of potential environment hazard of heavy metal to groundwater

Heavy metal pollution of soil and groundwater could be close associated. Once soil is polluted by heavy metal, heavy metal ion may be leached out gradually by the action of precipitation or irrigation and move down into groundwater. Possibilities for predicting long-term environmental hazards of heavy metals are limited. Due to the complexity of soil system and variability of numerous influencing factors, long-term prognosis on the mobilization of heavy metals in soils is highly uncertain [32]. Despite the large uncertainties involved, predictions of metal mobility from laboratory leaching experiments allow a range of results to be obtained under plausible assumptions and thus may support decisions [33]. According to the result of this study, it can be concluded that once soil is polluted by wastewater containing Pb and Cd, Pb and Cd tend to accumulating in topsoil quickly and not easily desorbing from soil, so they will move downward to groundwater very slowly. Considering adsorption/desorption amounts of Pb/Cd, Cd was more movable than that of Pb. Compared with Pb and Cd, the mobility of Cr(VI) in soil/groundwater system is much great because of its lesser adsorption capacity on soils. The column leaching experiment further proved that the mobility of heavy metal to groundwater decreased in the order of Cr(VI) \gg Cd > Pb, which was consistent with the result concluded from static adsorption/desorption. According to the relationship of static adsorption and column leaching experiment, it could be concluded that for the three contaminated farmland soil, the potential environment hazard of Pb and Cd to

groundwater followed the order of soil B > Soil C > Soil A, soil B > Soil A > Soil C respectively and the difference of potential environment hazard of Cr(VI) was not obvious.

4. Conclusions

Langmuir and Freundlich models gave good fits to the adsorption data of Pb and Cd for three tested soils. The data of Cr(VI) adsorption followed linear adsorption isotherm in the concentration range investigated. The adsorption amounts of heavy metals on the three soils followed the order: Pb > Cd \gg Cr(VI). The three soils had differences in adsorption abilities for Pb, Cd or Cr(VI), respectively. Pb, Cd adsorption and desorption on the three soils was fast. The adsorption amounts of Pb and Cd on the three soils were increased with pH value and the adsorption amounts of Cr(VI) were decreased. At pH value from 2.0 to 8.0, the desorption amounts of Pb and Cd were few. According to the results, Pb and Cd adsorbed greatly by topsoils were immobilized and move downward into groundwater very slowly. But Cr(VI) had high mobility and may move fast to groundwater. The result of long-term column leaching tests about mobility of heavy metals in aeration was in accord with the prediction of adsorption/desorption experiment.

Acknowledgement

This research was funded by the National Basic Research Program of China under Grant No. 2004CB418505.

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