SORPTION AND DESORPTION CHARACTERISTICS OF CADMIUM BY FOUR DIFFERENT SOILS IN NORTHEAST CHINA

ZHANG Lei[1, 2], SONG Feng-bin[1]

(1. Northeast Institute of Geography and Agricultural Ecology, Chinese Academy of Sciences, Changchun 130012, P. R. China;
2. The Graduate School of Chinese Academy of Sciences, Beijing 100039, P. R. China)

ABSTRACT: Four soils, phaeozem (PM), saline-alkali soil (SA), meadow albic bleached soil (MA) and dark brown forest soil (DB) from Northeast China were used to examine the sorption and desorption characteristics of Cd and pH influence on it. According to sorption experiment without pH control, the order of amount of absorbed Cd by soils was: SA>PM>DB>MA. The results from non-linear fitting method showed that Langmuir and Freundrich models were more adaptable than Temkin model in describing the sorption data. The maximum sorption amounts from Langmuir model were: PM>SA>MA>DB. Exponential equation for PM and SA and quadratic equation for MA and DB were suitable to fit the desorption data. The order of average desorption percentage was: MA>DB>PM>SA. The amounts of sorption by PM, DB and MA reached the maximum in pH 9.0, while sorption by SA was linearly increased in the experimental range of pH 3.3–11.4. In uniform pH, however, Cd sorption by SA was the minimum among four soils, which indicated that the more amounts of Cd absorbed by SA in isotherm sorption were ascribed to the higher soil pH. The higher sorption of Cd in PM resulted from the higher percentage of organic matter and clay components.

KEY WORDS: cadmium; soil; sorption; desorption; Northeast China

1 INTRODUCTION

As a persistent and toxic pollutant, cadmium (Cd) can result in many adverse health effects in a variety of tissues and organs such as the lung, kidney, urinary, bladder, pancreas, breast and prostate (SATARUG et al., 2003). Cadmium in soil transferring into edible parts of plant by root uptake can be accumulated in human bodies via food chain. Accordingly, reducing the cadmium uptake by roots has been one of the focuses of environmental science. Sorption and desorption are the most important chemical processes affecting the distribution of cadmium between the solid and the solution phases and the bioavailability of cadmium (HOLM et al., 1996). The sorption process is strongly affected by soil chemical and physical properties. For different soils, Cd sorption is significantly different due to different soil properties (CHEN, 1988).

Northeast China, one of the most important agricultural regions in China, has a traditional predominance in foodstuff-production and export of corn for a long time. But, as a heavy industry base in the past, the soil in Northeast China has been contaminated by heavy metal (GUO et al., 2005; YU et al., 2002), especially cadmium pollution (GUO and ZHOU, 2004). Furthermore, Cd contamination of agricultural soil due to industrial sludges, sewage waste, usage of fertilizers, pesticides, and atmospheric deposition has still potentially adverse effects on the quality and safety of food in Northeast China. Many studies on the sorption and desorption of Cd by soils have been carried out. However, there are few studies on Cd sorption and desorption by the agricultural soil in Northeast China and their comparison. The present study was conducted to investigate and analyze sorption and desorption characteristics of Cd by four typical agricultural soils in Northeast China, with the aim of providing scientific foundation for prevention of Cd contamination.

2 MATERIALS AND METHODS

2.1 Soil

The four soil samples used in this study were phaeozem (PM), saline-alkali soil (SA), meadow albic bleached soil (MA) and dark brown forest soil (DB) taken from Changchun, Baicheng, Dunhua of Jilin Province and Tongjiang of Heilongjiang Province, respectively. They were all important agricultural soils in Northeast China. The samples from 0–20cm of the topsoil layer were dried in air and sieved to 1mm for determining soil properties. Then, soil samples from several soil types were again sieved to 0.3mm for determination of sorption characteristics. Soil chemical properties were measured by using the method recommended by LU (1999). The soil properties are listed in Table 1.

2.2 Sorption Isotherms

Cd sorption by each soil type was determined by a batch equilibrium experiment. Soil samples of 1g were weighed and put into 50mL-plastic centrifuge tubes containing 0.4 0.8 1.6 2.4 4.0 6.4 9.6 16.0 32mg/L of $CdCl_2$ respectively. Ionic strength in the soil suspension was adjusted to 0.01M by $NaNO_3$. The ratio of soil-water was 1:40. Soil suspension was shaken for 12h at $25\pm$℃ in a shaker bath, and then equilibrated 6h to ensure sorption equilibrium (WANG *et al.*, 2001). Samples were centrifuged at 5000rpm for 10min and the Cd concentration in supernatant was determined. Amount of Cd adsorbed by the soils was calculated from the difference between the initial and final concentrations of metals in the equilibrium solution.

Table 1 Physical and chemical properties of selected soils

	pH	Organic matter (%)	CEC (cmol/kg)	Particle size (%)			Total Cd (mg/kg)
				1.00–0.05mm	0.050–0.002mm	<0.002mm	
Phaeozem (PM)	6.8	3.84	29.04	1.91	34.33	63.76	0.042
Saline-alkali soil (SA)	9.7	1.45	26.22	35.36	40.08	24.56	0.039
Meadow albic bleached soil (MA)	6.6	3.99	28.08	3.94	39.36	56.70	0.068
Dark brown forest soil (DB)	6.2	4.48	22.50	25.10	28.47	46.44	0.060

2.3 Desorption

The soil residue from isotherm sorption experiment was washed by distill water (25ml for each time), which was conducted three times until there was no Cd in the solution. And 25mL of 1M $NaNO_3$ solution was added in the residue after washed and shaken for 12h at $25\pm$℃ in shaker bath and centrifuged for 10min for determining Cd concentration.

2.4 Influence of pH

pH of the solution was adjusted by either 1M NaOH or 1M HNO_3 solutions. Cd concentration and ionic strength in the solution were adjusted to a same concentration of 10mg/L and 0.01M for each tube, respectively. After shaken for 12h and equilibrated 6h, soil suspension was centrifuged and the pH and Cd concentration in the supernatant were determined.

2.5 Determination of Cd

Some soil samples were digested in mixture of HNO_3-HF-$HClO_4$. Cd concentrations of both soils and solutions were determined by inductively coupled plasma spectrometry (ICPS-7500, Shimadzu, Japan). Accuracy of the Cd analysis was checked by comparison with certified standard soil samples GBW07401 (GSS-1). The

recovery of Cd was 89.24%. Results of determination in reference materials are in the certified range.

3 RESULTS AND DISCUSSION

3.1 Characteristics of Sorption Isotherm

The sorption of Cd on each soil type increased with the increasing of equilibrating concentration. But there were differences among four soils (Fig. 1). SA had the highest sorption amount and absorbed Cd increased linearly in the range of added Cd concentration. PM showed the same trend, but Cd amount absorbed by PM was lower than that of SA. Cd sorption by MA and DB increased significantly at the low equilibrium concentration. However, with the increase of Cd concentration, the isotherms of DB and MA gradually reached sorption plateaus, indicating that the sorption by two soils was close to the maximum. On average, SA with its alkaline nature had the highest sorption, followed by PM, DB and MA. According to previous studies (ANDERSON and CHRISTENSEN, 1988; CHRISTENSEN, 1989), pH was the most important factor that affects Cd sorption by soil. Clay minerals, oxides and organic matter played a key role in sorption of Cd. Soil pH was the first control factor in Cd mobility because pH influ-
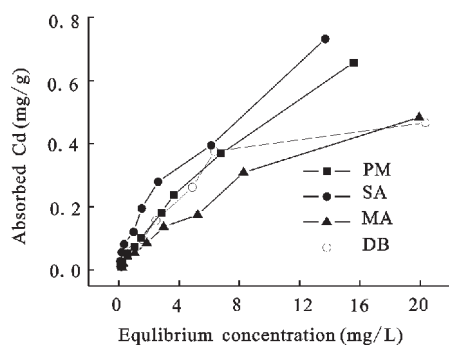
Fig. 1 Isothermal curves of Cd absorbed
by four soils in Northeast China

enced the availability of ligands in the solution. When soil pH increased, the sorption of Cd by soils was elevated significantly (ABOLLINO et al., 2003). The pH of SA was the highest in four soils, so pH may be the key factor of highest amount of Cd absorbed by SA.

It was noticeable that no significant difference was observed between PM and DB when added Cd concentration was low. However, in higher Cd concentration, Cd amount absorbed by PM was far more than that by

DB. It was shown that PM had a higher potential in Cd sorption than DB. The phenomenon above may ascribe to high proportion of clay minerals in PM. The surface charge density of soil particles affected sorption of Cd. The 2:1 clay minerals can absorb more Cd due to its higher CEC (NAIDU et al., 1997).

The most common Langmuir, Freundlich and Temkin models were applied to describing the sorption data.

Langmuir: $Y = X k X_m /(1+kX)$ (1)

Frendrich: $Y = k X^{1/a}$ (2)

Temkin: $Y = a + k \log X$ (3)

where, Y is Cd amount absorbed by the soils (mg/kg), X is Cd concentration in equilibrium solution (mg/L), and X_m is the adsorption maximum. The k and a denote constants of equations.

A non-linear fitting method using Levenberg-Marquardt (LM) arithmetic from Microcal Origin 7.0 was conducted to fit the sorption data. Compared with the linear fit method, it is more reliable because there are no transforms of isotherms (CHU et al., 2003; ZHANG et al., 2004). The results were listed in Table 2.

Table 2 Non-linear fitting parameters of Langmuir, Freundrich and Temkin models for Cd
sorption by the four soils in Northeast China

Soil type	Langmuir			Freundrich			Temkin		
	X_m	k	χ^2	k	a	χ^2	k	a	χ^2
PM	1.749	0.039	2.5E-4	0.075	1.256	4.4E-4	0.127	0.129	1.1E-2
SA	1.204	0.103	1.5E-3	0.137	1.579	5.0E-4	0.120	0.231	1.0E-2
MA	0.943	0.053	2.4E-4	0.061	1.427	4.0E-4	0.097	0.088	4.4E-3
DB	0.644	0.135	2.1E-4	0.096	1.841	1.0E-3	0.088	0.128	3.2E-3

As shown in Table 2, all three models fitted well the data. But according to χ^2, Langmuir and Freundrich models with the minor χ^2 values were more suitable than Temkin model to describe the Cd sorption by four soils (Table 2). According to X_m given by Langmuir model, the order of Cd maximum sorption by four soils was: PM>SA>MA>DB. Some studies have reported that organic matter affected greatly the process of Cd sorption by soils (KOOPAL et al., 2001). The many negatively charged functional groups on humic substances served as binding sites for positively charged metals, such as Cd (WEBER, 1988). SAUVÉ et al. (2000) reviewed and compiled data from more than 70 study papers and found from multiple linear regression analysis that soil organic matter following pH as the second component significantly affected the Cd sorption. Moreover, soils with more clay minerals can absorb more Cd (AUTIER and WHITE, 2004). The largest amount of Cd absorbed by PM contributed to the high proportion of clay minerals (63.76%) and organic

matter (3.84%).

In Freundrich equation, k was a measurement of capacity of adsorption, representing the proportion to the equilibrium constant of ions sorption and a could be considered as a measurement of the intensity of adsorption force (LIN and XUE, 1991). However a in the equation showed a negative influence on amount of Cd absorbed. Table 2 illustrated the order of a: DB>SA> MA>PM and the order of k: SA> DB>PM>MA.

3.2 Desorption Characteristics

The sorption of metal ions in soils can be classified into two parts: electric sorption (non-specific sorption) and specific sorption. Cd^{2+} that absorbed by the soil particles could be replaced by Na^+, K^+ and Ca^{2+} from the soil solid phase and entered into the solution again (WU, 1985). The more the amount of Cd were replaced by $NaNO_3$, the less the stabilization of Cd absorbed by the soil solid. Desorbed Cd showed more availability to plant in Cd-contaminated soils.

With the increase of soil Cd sorption amount, Cd desorbed in the soils was significantly increased (Fig. 2). Through fitting the four curves with a non-linear fitting method, it was found that exponential equation was suitable for PM and SA and quadratic equation was suitable for MA and DB, respectively. The equations were as follows ($R^2 > 0.998$):
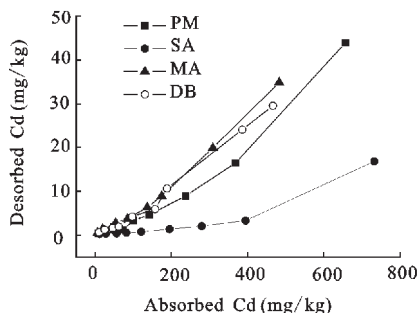
Fig. 2 Desorption curves of Cd on four
soils in Northeast China

PM: $Y = -12.5737 + 12.4386 \exp$
$(X/434.0872)$ (4)

SA: $Y = -0.3309 + 0.6662 \exp(X/225.2513)$ (5)

MA: $Y = 7E-05X^2 + 0.0406X + 0.1682$ (6)

DB: $Y = 5E-05X^2 + 0.0416X - 0.2013$ (7)

where Y (mg/kg) is the amount of desorbed Cd and X (mg/kg) is the amount of absorbed Cd before desorbed.

Unlike the sorption isotherms, desorption curves for DB and MA were higher than PM and SA. It suggested that the proportions of specific sorption in MA and DB were less than those in PM and SA, and Cd absorbed by MA and DB were easy to be desorbed. On average, the order of the amount of desorbed Cd for four soils was: PM>DB≈MA>SA. The greater amount of desorbed Cd by PM was due to the more Cd amount absorbed.

For all four soils, electric sorption had a small percentage (less than 10%) (Fig. 3). The order of average desorption percentage was: MA>DB>PM>SA, which was contrary to the result of isotherm experiment. Therefore, the conclusion can be given that Cd was easier to be adsorbed by PM and SA, and more difficult to be desorbed. Cd in DB and MA had more bioavailability than in PM and SA. Interestingly, desorption percentage of Cd for four soils was decreased initially and increased afterwards. It may be that the less absorbed Cd under condition of low desorbed Cd resulted in higher relative percentage and absolute amount of desorbed Cd increased under condition of high Cd absorbed. But the mechanism of soil sorption and desorption needed to be studied further.
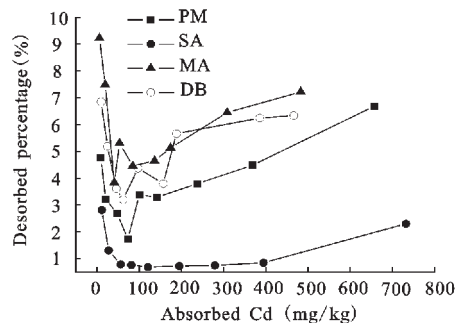
Fig. 3 Desorption percentage of Cd on
four soils in Northeast China

3.3 Influence of pH on Cd Sorption

It can be seen that Cd absorbed by four soils increased sharply with increase of pH from 3.6 to 11.4 (Fig. 4). The amounts of Cd absorbed by PM, SA, MA and DB were elevated by 306.9%, 431.7%, 332.7% and 315.4% in the range of pH 3.3–11.4, respectively, which was accordance to many previous studies (SAUVÉ et al., 2000; ALTIN et al., 1999). The process of specific sorption of Cd in soil colloid particle surfaces was accompanied by releasing of H^+ and it can be accelerated in a high pH environment. Cd absorbed by PM, MA and DB reached the highest amount at pH of approximately 9.0, and then reduced with the increase of pH. But the amount of Cd absorbed by SA increased linearly in all range of pH 4–12.
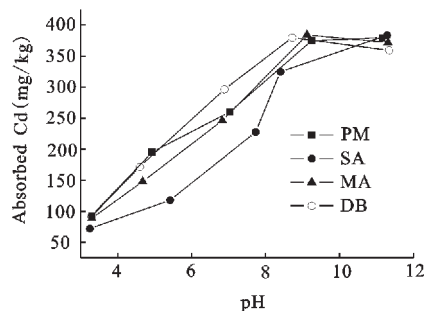
Fig. 4 Effects of pH on Cd absorbed by
four soils in Northeast China

It was noticeable that unlike the isotherm sorption, the quantity of Cd absorbed by SA was the minimum among four soils under the same pH. This phenomenon further proved that the more amount of Cd absorbed by SA in isotherm sorption condition was due to the higher pH of SA.

4 CONCLUSIONS

In isotherm sorption experiment, the order of amounts

of absorbed Cd by soils was: SA>PM>DB>MA. The result of non-linear fitting showed that Langmuir and Freundrich models were suitable in describing the sorption data. The maximum sorption amount from Langmuir model in four soils was: PM>SA>MA>DB.

Exponential equation for PM and SA and quadratic equation for MA and DB were suitable to fit the desorption data. The order of average desorption percentage in four soils was: MA>DB>PM>SA. Cd was easier to be adsorbed by PM and SA, and more difficult to be desorbed. Cd in DB and MA had more bioavailability than that in PM and SA.

Cd absorbed by four soils was sharply increased with the increase of pH. The amount of Cd absorbed by SA was the minimum among four soils under the same pH. It proved that the more amount of Cd absorbed by SA in isotherm sorption experiment was due to the higher pH of SA.

REFERENCES

ABOLLINO O, ACETO M, MALANDRINO M, 2003. Adsorption of heavy metals on Na-montmorillonite, effect of pH and organic substances [J]. *Water Research*, 37(7): 1619−1627.

ALTIN O, OZBELGE O H, DOGU T, 1999. Effect of pH, flow rate and concentration on the sorption of Pb and Cd on montmorillonite I. Experimental [J]. *Journal of Chemical Technology and Biotechnology*, 74(12): 1131−1138.

ANDERSON P R, CHRISTENSEN T H, 1988. Distribution coefficients of Cd, Co, Ni and Zn in soils [J]. *Journal of Soil Science*, 39: 15−22.

AUTIER V, WHITE D, 2004. Examination of cadmium sorption characteristics for a boreal soil near Fairbanks, Alaska [J]. *Journal of Hazard Materials*, 106(2−3): 149−155.

CHEN Huai-man, 1988. Adsorption and desorption of cadmium in soils. I. the influence of soil components on Cd adsorption and desorption [J]. *Acta Pedologica Sinica*, 25(1): 66−74. (in Chinese)

CHRISTENSEN T H, 1989. Cadmium soil sorption at low concentrations: VII. Correlation with soil parameters [J]. *Water Air Soil Pollution*, 44: 71−82.

CHU Zhao-sheng, LIU Wen-xin, TANG Hong-xiao, 2003. The sorption of isotherms of neodymium (III) and cerium (III) on loess at different pH values [J]. *Acta Scientiae Circumstantiae*, 23(2): 211−215. (in Chinese)

GUO Guan-lin, ZHOU Qi-xing, 2004. Contaminative trends of heavy metals in phaiozem of Northeast China [J]. *Journal of the Graduate School of the Chinese Academy of Sciences*, 21 (3): 386−392. (in Chinese)

GUO Ping, XIE Zhong-lei, LI Jun *et al.*, 2005. Relationships between fractionations of Pb, Cd, Cu, Zn and Ni and soil properties in urban soils of Changchun, China [J]. *Chinese Geographical Science*, 15(2): 179−185.

HOLM P E, ANDERSEN B B H, CHRISTENSEN T H, 1996. Cadmium solubility in aerobic soils [J]. *Soil Science Society of America Journal*, 60: 775−780.

KOOPAL W C, RIEMSDIJK VAN W, KINNIBURGH D, 2001. Humic matter and contaminants. General aspects and modeling metal ion binding [J]. *Pure and Applied Chemistry*, 73(12): 2005−2016.

LIN Yu-suo, XUE Jia-hua, 1991. Using of Freundlich equation for studying mechanism and movement of Zn added in calcareous soil [J]. *Acta Pedologica Sinica*, 28(4): 390−395. (in Chinese)

LU Ru-kun, 1999. *Analysis Methods for Soils and Agricultural Chemistry* [M]. Beijing: China Agricultural Science and Technology Press.

NAIDU R, KOOKANA R S, SUMNER M E, 1997. Cadmium sorption and transport in variable charge soils: a review [J]. *Journal of Environmental Quality*, 26: 602−617.

SATARUG S, BAKER J R, URBENJAPOL S, 2003. A global perspective on cadmium pollution and toxicity in non-occupationally exposed population [J]. *Toxicology Letters*, 137(1−2): 65−83.

SAUVÉ W, HENDERSHOT W, ALLEN H E, 2000. Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden and organic matter [J]. *Critical Reviews in Environmental Science and Technology*, 34 (7): 1125−1131.

WANG Hong, ZHOU Wei, LIN Bao, 2001. Effect of calcium carbonate on adsorption and desorption of cadmium in soils [J]. *Acta Ecologica Sinica*, 21(6): 932−937. (in Chinese)

WEBER J H, 1988. Binding and transport of metals by humic materials [A]. In: FRIMMEL F H, CHRISTMAN R F (eds.). *Humic Substances and Their Role in the Environment* [C]. New York: John Wiley and Sons Inc. 165−178.

WU Mei-ling, 1985. Specific adsorption of heavy metal ions on soil mineral colloid surface with variable electric charge [J]. *Chinese Journal of Soil Science*, 16(2): 89−94; 16(3): 138−141. (in Chinese)

YU Jun-bao, LIU Jing-shuang, WANG Jin-da *et al.*, 2002. Spatial-temporal variation of heavy metal elements content in covering soil of reclamation area in Fushun Coal Mine [J]. *Chinese Geographical Science*, 12(3): 268−272.

ZHANG De-jian, WEI Xian-xun, ZENG Guang-ming, 2004. The sorption isotherms of lead ion by sludge ramification adsorbent on the basis of non-linear fit [J]. *Ion Exchange and Adsorption*, 20(1): 1−6. (in Chinese)