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Adsorption-Desorption Characteristics of Cadmium in Variable Charge Soils

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Cadmium (Cd) has received considerable attention because of its association with various human health problems. The behavior of adsorption-desorption of Cd at contaminated levels in two variable charge soils were investigated. The red soil (RAR) developed on the Arenaceous rock (clayey, mixed siliceous thermic typic Dystrochrept) adsorbed more Cd^{2+} than the red soil (REQ) derived from the Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult). The characteristics of Cd adsorption could be described by the Freundlich equation ($r^2 = 0.997$ and 0.989, respectively, for the RAR and REQ) and the simple Langmuir adsorption equation ($r^2 = 0.985$ and 0.977, respectively, for the RAR and REQ). The maximum adsorption values (X_m) that were obtained from the simple Langmuir model were 36.23 mmol Cd^{2+} kg^{-1} soil and 31.15 mmol Cd^{2+} kg^{-1} soil, respectively for the RAR and REQ. Adsorption of Cd^{2+} decreased soil pH by 1.28 unit for the RAR soil and 1.23 unit for the REQ soil at the highest loading. The distribution coefficient (k_d) of Cd in the soil decreased exponentially with increasing Cd^{2+} loading. The adsorption of cadmium in the two variable charge soils was characterized by a rapid process that lasted approximately 15 min, followed by a slower but longer period. 85.5% and 79.4% of the added Cd were adsorbed within two hours by the RAR and REQ soil, respectively. More Cd^{2+} was adsorbed at 10°C than at 25°C or 40°C. After five successive desorptions with 0.01 mol L^{-1} $NaNO_3$ solution, 53.3% of the total adsorbed Cd^{2+} in the RAR soil was desorbed and the corresponding value of the REQ soil was 46.5%, indicating that the RAR soil had a lower affinity for Cd^{2+} than the REQ soil at the same Cd^{2+} loading.

Key Words: Adsorption-desorption characteristics; Cadmium, Soil pH, Temperature effect; Variable charge soils.

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INTRODUCTION

Toxic effects of heavy metals on plants, animals, and human beings have been well documented in the last two decades. Cadmium is a nonessential heavy metal pollutant of the environment, and it has been considered as an extremely important pollutant due to its high toxicity and great solubility in water.[1] It is listed by the United States Environmental Protection Agency (USEPA) as one of the 126 priority contaminants and as a human carcinogen by the International Agency for Research on Cancer (IARC, 1994).

The concentrations of Cd in uncontaminated soils of natural ecosystems are mainly affected by Cd contents in the parent materials.[2] Cadmium content of common rocks varies from 0.17 mg kg^{-1} in igneous rocks to 2.6 mg kg^{-1} in sedimentary rocks.[3]

Inputs of heavy metals, as a result of human activity, may damage or alter both natural and managed ecosystems.[4] Cadmium at contaminated levels can cause toxic effects on biological systems,[5,6] such as genotoxicity and exotoxicity in plants and animals.[7−10] The symptoms of cadmium toxicity are easily identifiable. In plants, the most general symptoms are stunting and chlorosis.[11] After being released to the environment, Cd rapidly enters biogeochemical cycles, which is bio-concentrated, and may eventually affect human health through the food chain. For instance, itai-itai is a disease caused by Cd-contaminated rice in Japan.[12−15]

Variable charge soils (Oxisols, Ultisols, Andisols, and some Alfisols) generally have low surface charge density with predominant pH-dependent charge.[16] Variable charge soils are widely distributed in southern China and other subtropical regions. Being highly weathered, these soils have a low pH; contain large amounts of Fe and Al oxides and kaolinite;[17] and carry mainly variable charge. Relatively limited information is available on behavior of Cd in variable charge soils.[18] In these soils, the nature of charged particle surface may vary with the composition of the ambient soil solution, and this may control both adsorption–desorption and the transport of heavy metals. Chemical interactions with soil surface are often masked by physical processes such as transport through preferential pathways.

The entry of a particular metal into the food chain is controlled by chemical behavior of the metal and properties of the soil. The heterogeneous nature of soils contributes to the complex and numerous equilibria that control the partitioning of Cd^{2+} between the aqueous and solid phases.[19] There are two general concepts regarding metal solubility in soil-water systems. The precipitation and dissolution of discrete solid phase minerals is a phase where metal ion concentration is a function of various solution parameters and the solubility product constant. The surface-chemically-controlled phase is a phase where the presence of insoluble phases with high surface areas and unique chemical properties provides sites for adsorption or interfacial reactions.[20] Variable charge

minerals such as Fe, Al, and Mn oxides carry charges varying from negative to positive, depending on pH.[17]

Metallic Cd and the divalent Cd ion are only slightly soluble in an aqueous solution when associated with phosphate and carbonate anions. Several investigators have indicated that adsorption onto clay minerals, metal oxides, organic matter, and whole soils is the predominate mechanism of heavy metal removal from dilute solution.[21-24] Understanding mechanisms of metal adsorption in soils is important as these reactions control the strength of the metal-soil surface interactions. Quantitative models are useful for comparing adsorption-desorption behavior of different soils under different operational conditions.[25] The most widely used models to describe the equilibrium behavior of metal adsorption are the Langmuir and Freundlich adsorption equations. The linear model of Freundlich is $X/M = K_fC^{1/N}$, and the linear Langmuir equation is $1/X = 1/Xm + 1/(Xm \times K) \times 1/C$, where X (mg kg^{-1}) is the amount of adsorbed ion, C (mg L^{-1}) is the concentration of the ion in equilibrium solution, N and K_f are conditional constants in the Freundlich equation, whereas Xm (maximum adsorption) and K (binding energy related constant) are conditional constants in the Langmuir equation.

John[26] found that organic matter in the soil contributed to increased Cd adsorption, which can be described by the Langmuir model. John[27] also observed that Cd adsorption parameters from the Langmuir equation were related to properties of 30 soils. In the 1970s, a "two-surface" Langmuir equation was also used to explain the adsorption of P, Zn ions.[28,29] A number of extractants including $CaCl_2$, $MgCl_2$, and HCl have been used for desorption of Cd^{2+} from soil, and the rate of desorption is generally high.[30,31]

Understanding surface sequestering processes in soils will allow us to evaluate the bioavailability and potential toxicity of trace metals to organisms, including human beings.[32] The overall objectives of this work were to investigate the adsorption-desorption of Cd in variable charge soils, which are widespread in China, and to understand the main factors that affect the surface reactions. A 0.01 mol $NaNO_3$ L^{-1} (pH 5.0) solution was used to evaluate desorption behavior of the adsorbed Cd.

MATERIALS AND METHODS

Soils Samples

The soils used in this study are two representative variable charge soils: the RAR soil (clayey, mixed siliceous thermic typic Dystrochrept), derived from Arenaceous rock, and the REQ soil (clayey, kaolinitic thermic plinthite Aquult), developed on Quaternary red earths. Soil samples were collected at 0 to 20 cm from Longyou County (119°02′~120°20′E, 28°44′~29°17′N), Zhejiang Province, southeastern China. Composite samples of the soils were air-dried, ground,

Table 1: Basic properties of the tested soils.

Items	RAR soil	REQ soil
pH (H_2O) (1 mol L^{-1}KCl)	5.31/3.69	4.77/3.42
Organic matter (g kg^{-1})	12.9	25.8
CEC (cmol kg^{-1})	21.15	15.59
Exchangeable acidity (cmol kg^{-1})	1.097	2.9
Exchangeable H^+ (cmol kg^{-1})	0.856	0.789
Exchangeable Al (cmol kg^{-1})	0.24	2.11
Particle composition (%)		
1–0.05 mm	56.97	9.86
0.05–0.01 mm	27.68	23.77
0.01–0.005 mm	4.07	13.92
0.005–0.001 mm	8.88	24.62
<0.001 mm	2.40	27.84

and passed through a 2-mm sieve prior to use. Some basic physicochemical properties of the soils are listed in Table 1.

Soil pH was measured using a pH meter (Thermo Orion 250, Orion Research, Inc., Boston, MA, USA) at a soil to solution ratio of 1:2.5 in both deionized water and 1 mol L^{-1} KCl. Soil organic carbon was determined by the modified Tinsley method.[33] Total exchangeable acidity and exchangeable Al^{3+} and H^+ were determined by the 1 mol L^{-1} extraction-titration method.[34] Particle size distribution was measured by the hydrometer method.[35] The CEC and exchangeable bases were determined using 1 mol L^{-1} NH_4Cl (pH 7.0) following the procedure described by Bao.[34] The concentrations of Cd in the extract or digest were measured using atomic absorption spectrometry (AAS) in an acetylene-air flame (AA6800, Shimadzu, Kyoto, Japan).

Adsorption of Cd^{2+} Ion

Portions of 1.0 g air-dried soil were weighed into 50-mL polypropylene centrifuge tubes, and 20 mL of 0.01 mol L^{-1} $NaNO_3$ (pH 5.0) solution containing 0, 10, 20, 40, 60, 80, 100, 150, 200, 250, 300 mg Cd L^{-1} [as $Cd(NO_3)_2$] were added to each tube. The suspensions were shaken at 200 rpm for 2 h at 25°C and equilibrated for an additional 22 h at 25°C in a dark incubator. No pH control was imposed. At the end of the designated time, the suspensions were centrifuged at 2000×g relative centrifugal force for 10 min and filtered though filter paper (quick mode). Ten mL of the filtrate were transferred into a 10-mL polypropylene centrifuge tube for measuring Cd^{2+} concentration using the AAS. Total amounts of adsorbed Cd^{2+} were calculated by the difference between the total applied Cd^{2+} and the solution Cd^{2+} in the equilibrium solution. The remaining solution was used for measuring pH.

For the kinetic experiment, the basic steps are similar with the adsorption experiment, except that the suspensions were shaken at 200 rpm at 25°C in a dark incubator, and at the intervals of 0, 5, 15, 30, 45, 60, 120, 240, 480,

600, 1200 minutes, subsamples of the suspensions were centrifuged and Cd^{2+} concentration in the supernatant solution was determined.

For the temperature effect experiment, the basic steps are similar to those of the adsorption experiment, and the only difference is that the equilibrium of Cd^{2+} adsorption was conducted at three different temperatures, i.e., 10°C, 25°C, and 40°C.

Desorption of Adsorbed Cd^{2+} Ion

The tube containing soil residue from the adsorption experiment after being separated from the supernatant solution was weighed to quantify residual Cd^{2+} trapped in the solution. Twenty mL of 0.01 mol L^{-1} $NaNO_3$ (pH 5.0) were added to each tube containing the Cd-enriched soil residue. The suspensions were shaken at 200 rpm for 2 h at 25°C and equilibrated for an additional 22 h. The equilibrated suspensions were then centrifuged at $2000 \times g$ relative centrifugal force for 10 min and filtered. Ten mL of the filtrate were transferred into a 10-ml polypropylene centrifuge tube for measuring Cd^{2+} concentration. The remaining solution was used for measuring pH. In order to estimate the affinity of Cd^{2+} in soils, the desorption process was repeated five times (D1 to D5). The non-extractable fraction of the adsorbed Cd^{2+} was obtained by the difference between the total adsorbed Cd^{2+} and the total recovered Cd^{2+} by the five successive extractions with the $NaNO_3$ solution (pH 5.0).[17]

The standard solution (GSB07-1276-2000 National Certified Reference Materials of China 103102) was used to prepare the working standard in laboratory, and the environmental reference materials (ERMs GSBZ 50009-88 National Certified Reference Materials of China 0119) were used at a frequency of once per 50 samples for quality assurance and quality control. All glassware and plastic-ware used in this study were previously soaked in 14% HNO_3 (v/v) and rinsed with deionized water. All reagents used were of analytical grade or better.

Statistical Analysis

All data were statistically processed using Microsoft Excel, and the regression and other statistical analyses were conducted using the programs of SAS 8.2.

RESULTS AND DISCUSSION

Adsorption Isotherms of Cd^{2+}

The adsorption characteristics of Cd^{2+} in the two variable charge soils were similar. Adsorption of Cd^{2+} increased steeply with Cd^{2+} concentration in the equilibrium solution at low concentrations ($0 \sim 10$ mmol kg^{-1}) for both soils, but
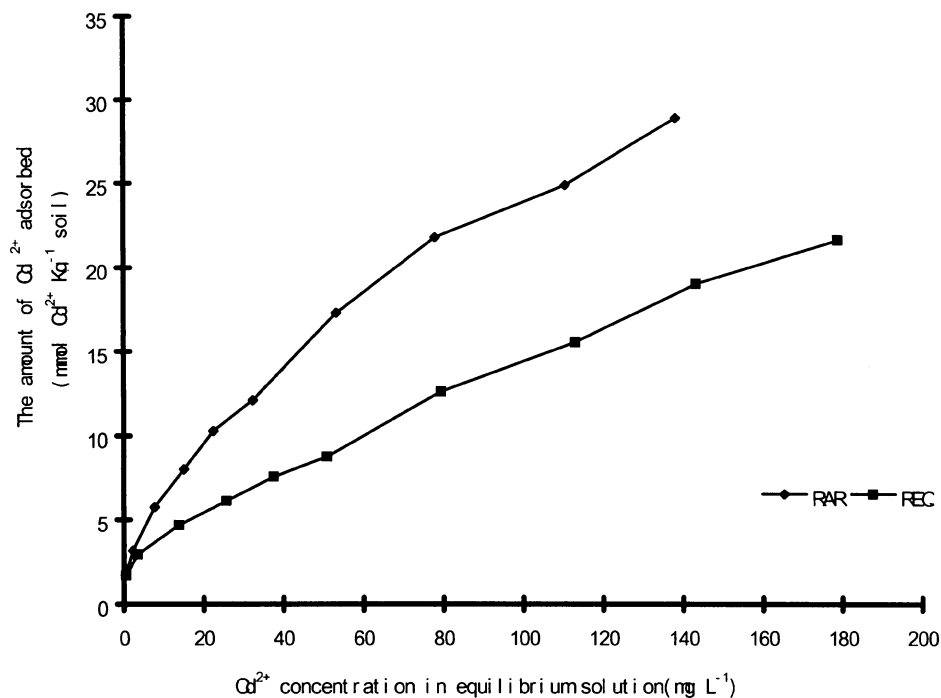
Figure 1: Isotherms of Cd^{2+} adsorption in the two variable charge soils. Data are means of three replications.

the increase diminished at the equilibrium Cd^{2+} concentrations > 10 mmol kg^{-1} (Fig. 1). Approximately half of Cd^{2+} applied at concentrations up to 300 mg L^{-1} was adsorbed in both soils. More Cd^{2+} was adsorbed in the RAR than the REQ soil at the same Cd^{2+} equilibrium concentrations. At the highest level of added Cd^{2+} (6000 mg kg^{-1}), the RAR soil adsorbed 53.94% of the applied Cd^{2+}, as compared with 40.41% for the REQ soil (Table 2), probably due to its higher CEC and pH (Table 1).

Cadmium adsorption in both soils was well described by the Langmuir equation with a correlation coefficient (r^2) 0.985 for the RAR and 0.977 for the REQ soils. The monolayer maximum adsorption (Xm) from the Langmuir equation is usually used for comparing potential adsorption capacity of different soils and soil components.[36] In this study, the Xm value was 36.23 mmol kg^{-1} for the RAR soil and 31.15 mmol kg^{-1} for the REQ soil. The physical meaning of K from the Langmuir equation is not well defined. However, it is usually considered to relate the binding energy of metal adsorption.[37] The RAR soil had a greater K value than the REQ soil (Table 3). The product of Xm and K (MBC $=$ Xm $\cdot$ K) from the Langmuir equation reflects the maximum buffer capacity of the soil for Cd^{2+}. The value of MBC was 0.65 and 0.28, respectively, for the RAR and REQ soil, suggesting that the RAR soil had a greater buffering

Table 2: The adsorption and desorption of Cd^{2+} in two variable charge soils.

Soil type	Cd^{2+} added (mg L^{-1})	Cd^{2+} desorbed with one mol $NaNO_3^{-1}$ (pH = 5.0)		
		Adsorption (%)[a]	Total desorption (%)[b]	First desorption (%)[c]
RAR soil	10	95.75	1.95	52.84
	20	88.48	7.32	38.30
	40	80.49	26.21	24.75
	60	74.84	32.89	26.85
	80	71.94	35.26	27.23
	100	67.66	38.10	26.66
	150	64.56	39.55	27.12
	200	61.03	39.48	26.51
	250	55.80	40.78	25.25
	300	53.94	40.49	24.77
REQ soil	10	94.20	8.47	41.63
	20	82.43	20.48	31.93
	40	65.41	32.16	35.53
	60	57.08	43.62	35.29
	80	53.04	47.45	35.91
	100	49.10	51.46	34.03
	150	47.06	53.82	34.53
	200	43.49	55.86	34.11
	250	42.68	54.53	33.24
	300	40.41	53.30	31.72

[a]Percentage of adsorbed Cd^{2+} in the total applied Cd^{2+}.
[b]Percentage of the desorbed Cd^{2+} by five successive extractions in the total adsorbed Cd^{2+}.
[c]Percentage of the desorbed Cd^{2+} by the first extractions in the total desorbed Cd^{2+}.

capacity for Cd^{2+} than the REQ soil (Table 3). A similar trend of Pb adsorption in these two soils was reported by Yang et al.[37]

Effect of Cd^{2+} Adsorption-Desorption on Soil pH

The pH of equilibrium solution significantly decreased during Cd^{2+} adsorption for both soils (Table 4). The pH of REQ soil decreased more than the RAR soil at the same Cd^{2+} loading. For the same soil, equilibrium solution pH decreased with increasing Cd^{2+} adsorption. The maximum pH drop was up to 1.28 unit for the RAR soil and 1.23 unit for the REQ soil. Obviously, H^+ and/or Al^{3+} were released during Cd^{2+} adsorption. Similar results were reported by Yu et al.[17] with Cu^{2+} adsorption and Yang et al.[37] with Pb^{2+} adsorption.

**Table 3:** Adsorption parameters of Cd^{2+} in the RAR soil and the REQ soil at 25°C.

Soil type	Langmuir equation $(1/X = 1/Xm + 1/(Xm \times K) \times 1/C)$			Freundlich equation $(X = K_F C^n)$		
	K_L (L $mmol^{-1}$)	Xm (mmol kg^{-1})	r^2	K_F (L kg^{-1})	N	r^2
RAR soil	0.018	36.23	0.985	1.73	0.57	0.997
REQ soil	0.009	31.15	0.977	0.84	0.62	0.989

Table 4: Equilibrium solution pH in relation to Cd^{2+} adsorption (ads) and successive desorptions (Des-1 to Des-5).

pH	Cd^{2+} concentration (mg kg^{-1})	Ads	Des-1	Des-2	Des-3	Des-4	Des-5
RAR soil	0	6.25	5.84	5.97	6.25	6.30	6.24
	10	6.16	5.86	5.77	6.33	6.22	6.23
	20	5.94	5.94	5.82	6.38	6.30	6.28
	40	5.77	5.84	5.81	6.26	6.24	6.20
	60	5.75	5.76	5.75	6.26	6.13	6.09
	80	5.72	5.78	5.73	6.28	6.08	6.10
	100	5.79	5.77	5.70	6.28	6.03	6.08
	150	5.46	5.63	5.81	6.22	6.01	6.08
	200	5.07	5.52	5.75	6.21	6.05	6.08
	250	5.11	5.54	5.72	6.19	6.00	6.10
	300	4.97	5.50	5.65	6.08	6.01	6.13
REQ soil	0	5.84	5.91	5.90	6.30	5.84	6.35
	10	5.79	6.01	5.98	6.18	5.97	6.31
	20	5.67	5.73	6.01	6.15	5.74	6.19
	40	5.4	5.59	5.77	6.05	5.84	6.15
	60	5.17	5.60	5.74	6.00	5.97	6.21
	80	5.09	5.71	5.78	6.13	5.81	6.30
	100	5.05	5.65	5.75	6.08	5.66	6.26
	150	4.86	5.54	5.70	6.15	5.86	6.19
	200	4.69	5.59	5.73	6.16	5.72	6.13
	250	4.61	5.54	5.67	6.07	5.62	6.16
	300	4.61	5.65	5.66	6.05	5.82	5.97

These results suggest that heavy metal contamination potentially causes soil acidification, and the more the heavy metal input, the more acute the acidification may be. The relationship between pH decrease and the amounts of Cd^{2+} adsorbed fitted well a multinomial regression equation with correlation coefficients $R^2 = 0.97$ and 0.98, respectively, for the RAR and REQ soil (Fig. 2).

After five desorptions, equilibrium solution pH increased gradually, probably because of H^+ retention during Cd^{2+} desorption. Equilibrium solution pH generally increased with desorption and was lower when Cd^{2+} concentration
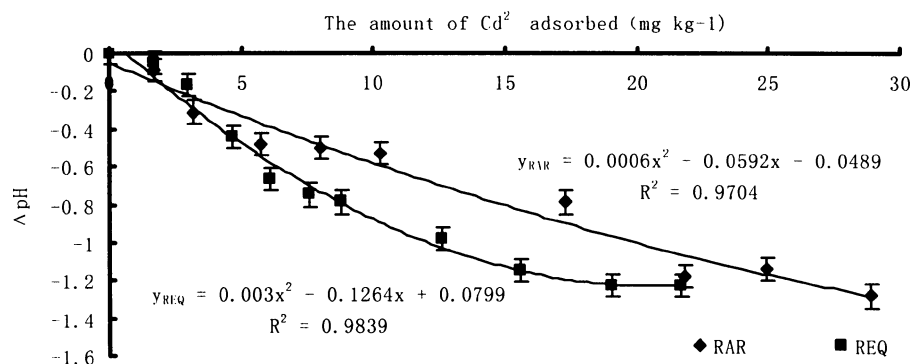
Figure 2: pH changes of the equilibrium solution in relation to Cd^{2+} adsorption in the two variable charge soils. Data are means of three replications.

in the equilibrium solution increased (Table 4). At low rates of added Cd^{2+} (<400 mg kg^{-1}), the pH tended to return to the initial level after desorption for both soils. However, the equilibrium solution pH was lower than the original at high initial Cd^{2+} concentrations, possibly because of some residual Cd^{2+} that was not desorbable. A greater decrease in equilibrium solution pH was observed in the RAR soil than the REQ soil, suggesting that different mechanisms may be involved in the Cd^{2+} adsorption in different soils.

The difference in Cd^{2+} adsorption between the two variable charge soils may be attributed to the higher CEC and soil pH of the RAR soil, as compared with the REQ soil (Table 1). These results were in agreement with previous report of Appel and Ma,[32] who suggested that metal adsorption was more dependent on clay type and CEC than amount of clay. Appel and Ma also indicated that soil pH plays a major role in the adsorption of heavy metals as it directly controls the solubility of metal hydroxides, as well as metal carbonates and phosphates. Increasing soil pH increases cationic heavy metal retention to soil surfaces via adsorption, inner-sphere surface complexation, and/or precipitation and multinuclear-type reactions.[16,36] Several studies on metal adsorption in soils have demonstrated close relationships between metal adsorption and soil pH or CEC.[38]

Distribution Coefficients of Cd^{2+}

The distribution coefficient K_d is defined as the ratio of adsorbed Cd^{2+} to dissolved Cd^{2+}. That is the ratio of heavy metal in solid phase to liquid phase. This parameter can reflect the affinity of heavy metal to soil surface.[39] The K_d values were high at relatively low Cd^{2+} additions, decreased greatly with increasing initial Cd^{2+} concentrations from 200 to 800 mg kg^{-1} for both soils, but slowly at higher Cd^{2+} concentrations (>800 mg kg^{-1}). This might be attributable to the high affinity of Cd^{2+} to some highly selective sites at low concentrations and low affinity for those less selective sites at high Cd^{2+} concentrations.[40] The RAR soil had a much higher K_d value than the REQ soil (Fig. 3). The difference may be attributed to the higher CEC and soil pH of the RAR soil, as compared with the REQ soil (Table 1).

The reaction of heavy metal adsorption on soils can be universally described as

$$S(OH)_n + M^{2+} = (S - OM)^{(2-n)+} + nH^+ \tag{1}$$
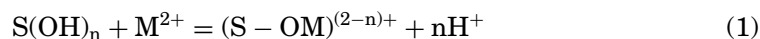
The linear form of Eq. (1) is expressed as

$$\log(Kd) = \log K' + npH \tag{2}$$

where Kd is the distribution coefficient; $K' = K \times a \times [S(OH)_n]$ is a constant; n is the average number of H^+ released for adsorption of one Cd^{2+}.

There was a linear relationship between the K_d value and equilibrium solution pH of adsorption or both soils ($r^2 = 0.977$ and 0.939, respectively, for the
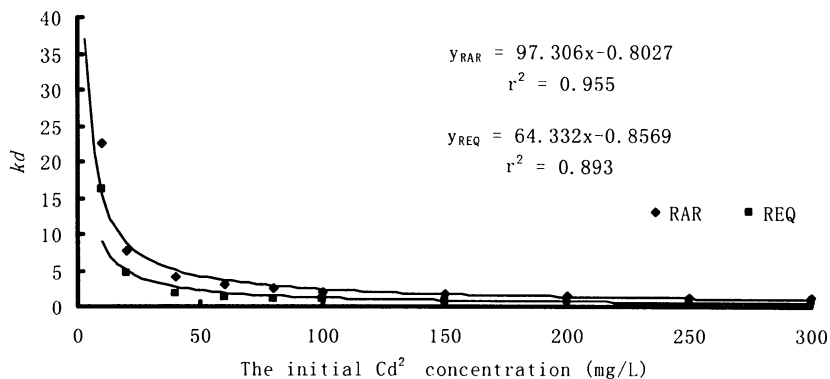
Figure 3: Effect of initial Cd^{2+} concentration on Cd^{2+} distribution coefficient (K_d) in the two red soils. Data are means of three replications.

RAR and REQ soil) (Fig. 4). For variable charge soils, H^+ is released mainly through specific adsorption of Cd^{2+}, with a small contribution from nonspecific adsorption process. Therefore, the adsorption of Cd^{2+} on the variable charge soil surface involves mainly specific adsorption, with a small portion of non-specific adsorption. These results suggest that even in the Fe and Al oxides-enriched soils, the adsorbed Cd still holds a certain degree of bioavailability. In this study, a greater n value was observed with the RAR soil (0.5525) than the REQ soil (0.3636). This agreed with the previous finding that the adsorption equilibrium pH of the RAR soil was much lower than that of the REQ soil and it decreased more rapidly with the amount of Cd^{2+} adsorbed.

Kinetics Characteristics of Cd^{2+} Adsorption

Cadmium adsorption increased with time for both soils (Fig. 5), but was characterized by a rapid stage followed by a slower adsorption stage. The
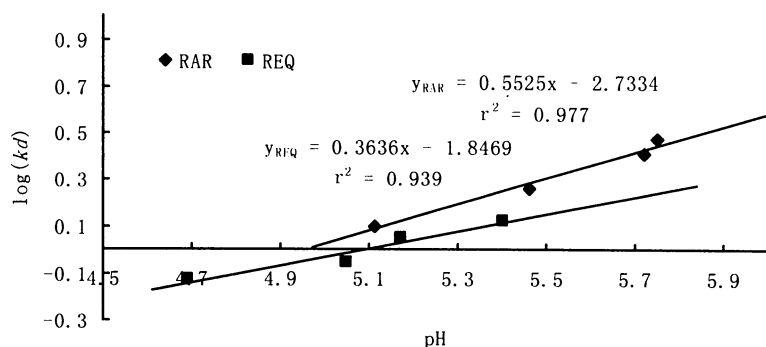

Figure 4: The relationship between K_d and pH of adsorption equilibrium. Data are means of three replications.
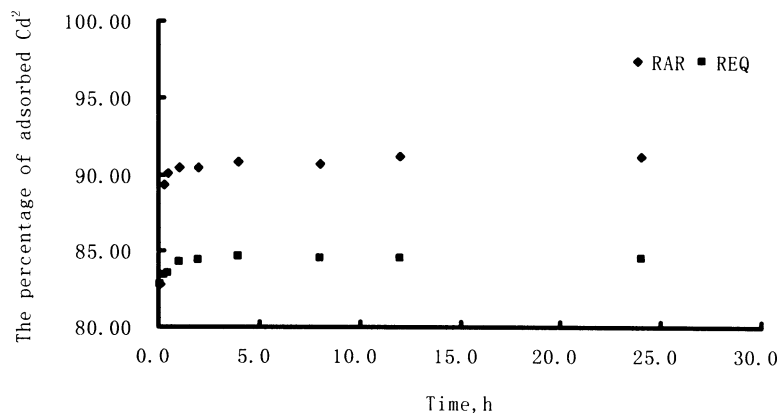
Figure 5: Kinetics characteristic of Cd^{2+} adsorption. Data are means of three replications.

equilibrium of rapid Cd^{2+} adsorption was achieved in 15 min and the slower stage lasted much longer but with minimal increases in Cd^{2+} adsorption. Most of the Cd^{2+} adsorption occurred within a few minutes of reaction, and the increase in Cd^{2+} adsorption was minimal after two hours. At the beginning of adsorption, Cd^{2+} quickly occupied adsorption sites with high binding energy. As the reaction time extended, Cd^{2+} adsorption diminished because of limited available sites that had relatively low affinity for Cd^{2+}. Tiller, Nayyar, and Clayton[40] observed that the Zn^{2+} adsorbed on the non-exchangeable sites tended to prevent Zn^{2+} to enter the exchangeable sites. Adsorption of Cd^{2+} may be of similar nature, which restricts the diffusion of cadmium into the granules of the soil.

The variable charge soils hold negative charge on the surface at common pH values (5–6). Due to the strong affinity between the negatively charged surface and the positively charged ion, Cd^{2+} reaches the surface of the soil colloids. In the meantime, the difference in electrical potential between the potential-ion layer and the diffuse layer is reduced. Consequently, the rate of Cd^{2+} entering adsorption sites decreases and the adsorption reaches the equilibrium when the potential difference decreased to zero, even negative. The adsorption of Cd^{2+} in this study was almost constant after two hours, suggesting that the diffusion of Cd^{2+} into the double-charge layer reached maximum.[41,42]

Effects of Temperature on Cd^{2+} Adsorption

There was a significant difference in Cd^{2+} adsorption at three different temperatures (Fig. 6). For both soils, Cd^{2+} adsorption was greater at 10°C than 25°C, and was the lowest at 40°C at the same Cd^{2+} equilibrium concentrations. The RAR soil adsorbed more Cd^{2+} at 10°C than at 25°C or 40°C, and the REQ soil had a similar result. At the highest level of added Cd^{2+} (2000 mg kg^{-1}), the RAR soil at 10°C adsorbed 67.8% of the applied Cd^{2+}, as compared with
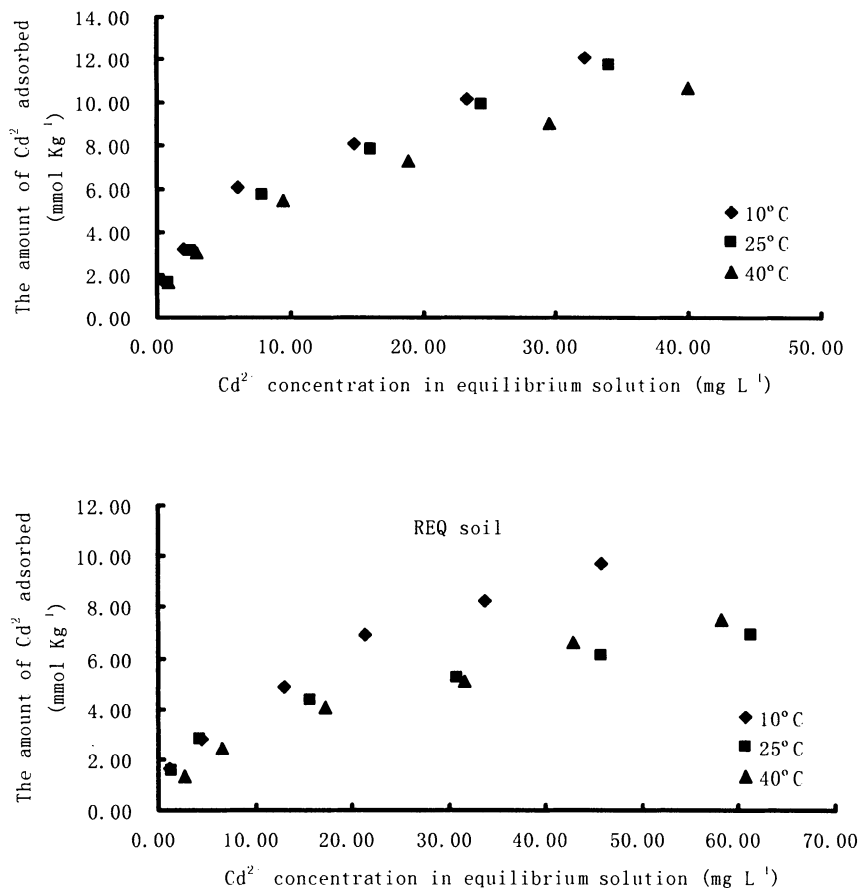
Figure 6: Thermodynamic characteristics of Cd^{2+} adsorption in two variable charge soils. Data are means of three replications.

65.9% at 25°C and 60.1% at 40°C, whereas the REQ soil adsorbed 54.3% of the applied Cd^{2+} at 10°C, as compared with 38.7% at 25°C and 41.9% at 40°C (Table 5). These results indicate that the adsorption process of Cd^{2+} is of exothermic nature. This may be attributed to an increased escaping tendency of the solute from the solid to the solution phase at raised temperatures.[43] Similar results were reported by Singh et al.[44]

Temperature did not affect the fitness of Cd^{2+} adsorption in both soils to the Langmuir $(1/X = 1/Xm + 1/(Xm \times K) \times 1/C)$ equation, with a good correlation coefficient $(r^2 > 0.96)$. The monolayer maximum adsorption values (Xm) from the Langmuir equation at the temperatures of 10°C, 25°C, and 40°C were 8.84, 10.96, and 8.64 mmol kg^{-1}, respectively, for the RAR soil and 7.23, 5.91, 8.03 mmol kg^{-1}, respectively, for the REQ soil (Table 6).

As can be seen in Figure 6, the adsorption isotherm curve of Cd^{2+} at 10°C was above that at 25°C or 40°C for both soils. However, the changes of Xm

Table 5: Adsorption of Cd^{2+} in two variable charge soils at different temperatures.

	Cd²⁺ added (mg L⁻¹)	10°C Qᵃ (mmol kg⁻¹)	%ᵇ	25°C Qᵃ (mmol kg⁻¹)	Pʸ %	40°C Qᵃ (mmol kg⁻¹)	%ᵇ
RAR Soil	10	1.698	95.1	1.632	91.4	1.625	91.0
	20	3.223	90.2	3.119	87.3	3.041	85.1
	40	6.047	84.7	5.718	80.1	5.450	76.3
	60	8.058	75.2	7.833	73.1	7.339	68.5
	80	10.137	71.0	9.921	69.4	9.007	63.1
	100	12.100	67.8	11.771	65.9	10.731	60.1
REQ Soil	10	1.594	89.3	1.555	87.1	1.294	72.4
	20	2.789	78.1	2.795	78.3	2.404	67.3
	40	4.823	67.5	4.329	60.6	4.075	57.1
	60	6.892	64.3	5.192	48.5	5.056	47.2
	80	8.258	57.8	6.128	42.9	6.633	46.4
	100	9.701	54.3	6.916	38.7	7.477	41.9

ᵃQ, adsorption value of Cd^{2+} in two red soils at different temperature (mmol kg⁻¹).
ᵇPercentage of adsorbed Cd^{2+} in two red soils at different temperature, %.

values with temperatures did not follow the same pattern. Similar trends were observed for K_L. This discrepancy may reflect the complex nature of Cd^{2+} adsorption in soils, with multiple mechanisms involved.[45]

The distribution coefficient *Kd* value was affected by temperature (Fig. 7). The *Kd* value was greater at 10°C than at 25°C or 40°C for both soils. Apparently, increasing temperature enhances Cd^{2+} desorption potential, thus reducing its adsorption.

Desorption of Adsorbed Cd^{2+}

The need to predict bioavailability of Cd^{2+} encourages more emphasis on desorption than adsorption. The portion of the Cd^{2+} adsorbed that was desorbed by desorptions was likely available to plants. So it is important to understand desorption characteristics of Cd^{2+} in soils.

Approximately half of the adsorbed Cd^{2+} was desorbed by the 0.01 mol L⁻¹ $NaNO_3$ (Table 2). The desorption increased with increasing Cd^{2+} adsorption

Table 6: Adsorption parameters of Cd^{2+} in the RAR soil and the REQ soil at different temperatures.

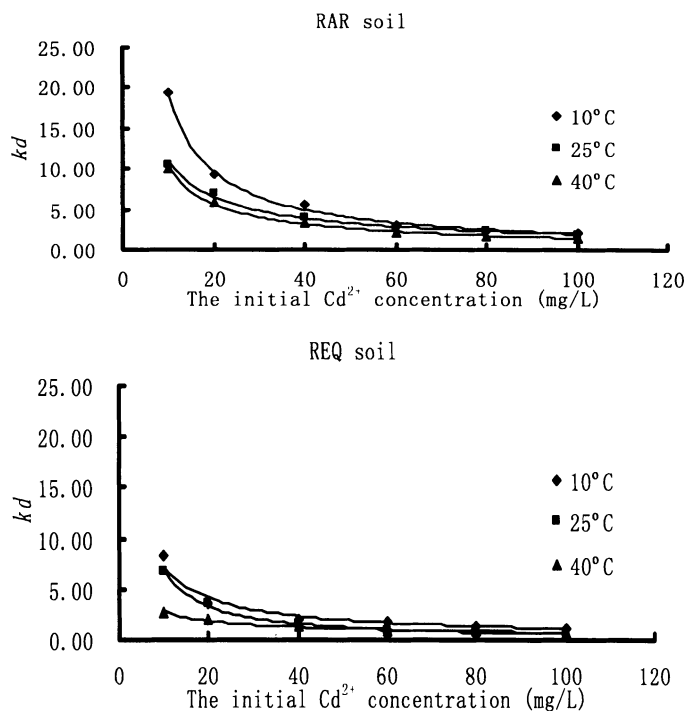| Soil type	Temperature (°C)	Langmuir equation $1/X = 1/Xm + 1/(Xm \times K) \times 1/C$ K_L (L mmol⁻¹)	Xm (mmol kg⁻¹)	r^2
RAR	10	0.47	8.84	0.96
	25	0.22	10.06	0.98
	40	0.25	8.64	0.97
REQ	10	0.25	7.23	0.93
	25	0.27	5.91	0.98
	40	0.07	8.03	0.99

RAR soil

REQ soil

Figure 7: Effect of initial Cd^{2+} concentration on Cd^{2+} distribution coefficient (K_d) in the two variable charge soils at different temperatures. Data are means of three replications.

saturation for both soils. The RAR soil desorbed less Cd^{2+} than the REQ soil at the same Cd^{2+} concentrations. After five successive desorptions, the total amounts of Cd^{2+} recovered by desorption accounted for 40.49% of the adsorbed Cd^{2+} for the RAR soil and 53.30% for the REQ soil (Table 2). The RAR soil that
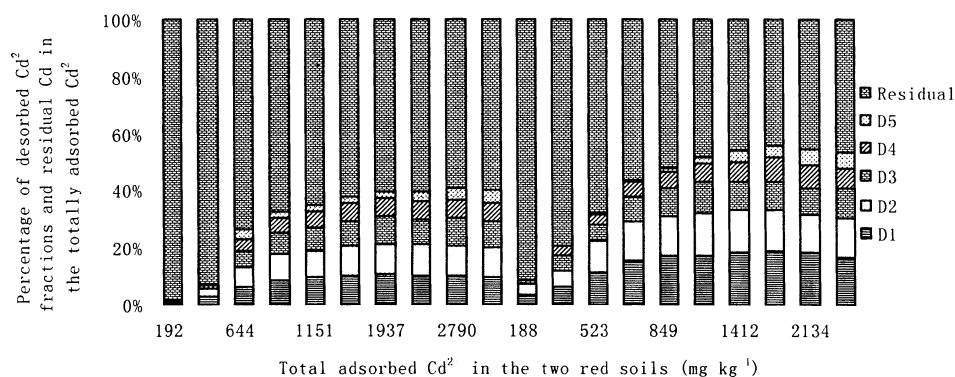
Figure 8: Fractions of successive desorptions and residual Cd in the total adsorbed Cd^{2+}. D1–D5 represents the fraction of desorbed Cd^{2+} from each of the five successive desorptions, and Residual represents the fraction of adsorbed Cd^{2+} not removed by successive desorption of 1 mol $NaNO_3$ L^{-1} (pH 5.0). Data are means of three replications.
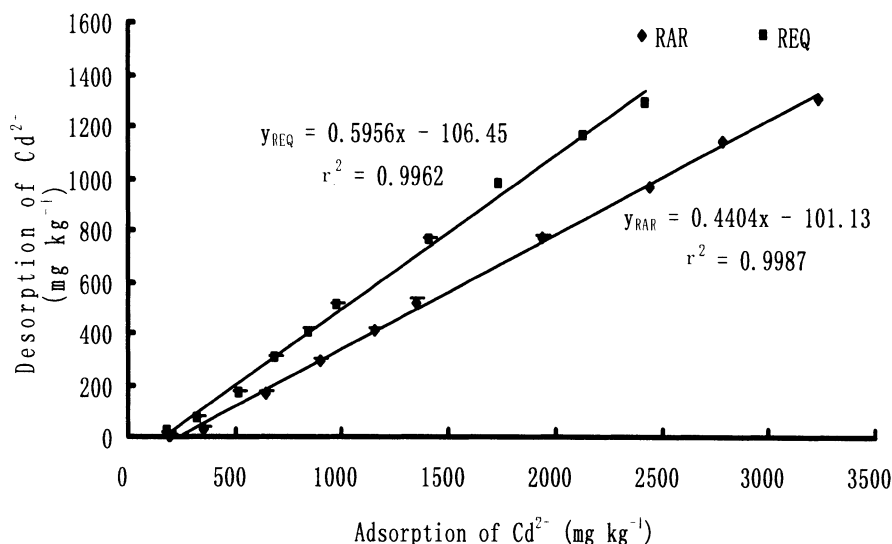
Figure 9: The relationship between Cd^{2+} adsorption and desorption. Data are means of three replications.

had a greater adsorption capacity desorbed less Cd^{2+} than the REQ soil at the same amount of adsorbed Cd^{2+}.

The proportion of the adsorbed Cd^{2+} that was not desorbed by the $NaNO_3$ decreased with the increasing concentration of adsorbed Cd^{2+} (Fig. 8). The portion of the Cd^{2+} adsorbed that was not desorbed by the five successive desorptions was likely related to high binding energy sites, and may not be available to plants.

There was a linear relationship between the amount of Cd^{2+} desorbed and the amount of adsorbed Cd^{2+} for both the RAR and REQ soils ($r^2 = 0.999$ and 0.998, respectively) (Fig. 9). Both the RAR and REQ soil retained a large amount of applied Cd^{2+}. This portion of residual Cd^{2+} after five successive desorptions measures the potential fixation of Cd^{2+} by the soils. This residual Cd^{2+} was calculated by the regression equation of adsorption-desorption relationship. The amount of residual Cd^{2+} was 1925.9 mg kg^{-1} for the RAR soil and 1132.4 mg kg^{-1} for the REQ soil. These results agree with the previous findings that Cd^{2+} was more tightly adsorbed in the RAR than the REQ soil.

CONCLUSIONS

The adsorption and desorption behavior of Cd^{2+} was well described by the Freundlich and the Langmuir models with correlation coefficients $r^2 > 0.977$. The RAR soil that contained greater amounts of exchangeable Al and Fe oxides, with a lower pH, had a greater adsorption capacity and affinity for Cd^{2+}

than the REQ soil. The adsorption of Cd^{2+} caused soil acidification. Equilibrium solution pH decreased with increasing Cd^{2+} adsorption. The pH decrease was greater in the REQ soil than in the RAR soil. The Cd^{2+} adsorption consisted of a rapid reaction that was completed in the first 15 min, and a slower and longer adsorption stage. The adsorption of Cd^{2+} in the two variable charge soils was observed to be an endothermic reaction. Cadmium adsorption decreased with increasing temperature. The 0.01 mol L^{-1} $NaNO_3$ (pH = 5.0) could release approximately half of the adsorbed Cd^{2+} from the two soils. The RAR soil retained more adsorbed Cd^{2+} than the REQ soil after five successive desorptions with the 0.01 mol L^{-1} $NaNO_3$.

ACKNOWLEDGMENTS

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