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Sorption–desorption of cadmium in aqueous palygorskite, sepiolite, and calcite suspensions: Isotherm hysteresis

Mehran Shirvani [a,*], Mahmoud Kalbasi [a], Hosein Shariatmadari [a],
Farshid Nourbakhsh [a], Bijan Najafi [b]

[a] *Department of Soil Science, College of Agriculture, Isfahan University of Technology, Isfahan, Iran*
[b] *Department of Chemistry, Isfahan University of Technology, Isfahan, Iran*

Abstract

Sorption isotherms have been widely used to assess the heavy metal retention characteristics of soil particles. Desorption behavior of the retained metals, however, usually differ from that of sorption, leading to a lack of coincidence in the experimentally obtained sorption and desorption isotherms. In this study, we examine the nonsingularity of cadmium (Cd) sorption–desorption isotherms, to check the possible hysteresis and reversibility phenomena, in aqueous palygorskite, sepiolite and calcite systems. Sorption of Cd was carried out using a 24-h batch equilibration experiment with eight different Cd solution concentrations, equivalent to 20–100% of maximum sorption capacity of each mineral. Immediately after sorption, desorption took place using successive dilution method with five consecutive desorption steps. Both Cd sorption and desorption data were adequately described by Freundlich equation $(0.81 < r^2 < 0.99)$. The sorption and desorption reactions, however, did not provide the same isotherms, indicating that hysteresis occurred in Cd sorption–desorption processes. The extent of hysteresis was quantified based on the differences obtained from sorption and desorption isotherms regarding the amount of Cd sorbed, the Freundlich exponent, and the Cd distribution coefficient. The results revealed that, sepiolite possessed the most hysteretic behavior among the minerals studied. Calcite showed much smaller hysteresis compared to the other two silicate clays at low Cd surface load, but its hysteresis indices significantly increased, and exceeded that of palygorskite, as the amount of Cd in the systems increased. The average amount of Cd released after five desorption steps, was 13.8%, 2.2% and 3.6% for the palygorskite, sepiolite and calcite, respectively, indicating that a large portion of Cd was irreversibly retained by the minerals.
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1. Introduction

Adsorption and desorption of heavy and trace metals on/from soil constituents are of the most important reactions determining the mobility and bioavailability of these elements in the environment. Sorption characteristics of various soil particles and minerals have been frequently studied through sorption isotherm experiments. A sorption isotherm represents the quantity of an ion (or molecule) sorbed by a solid as a function of the equilibrium concentration of that ion in solution, at a constant temperature.

Desorption of the sorbed ions from the solid phase actually controls the availability and leachability of those ions in soils. Distribution and retardation coefficients of chemicals entered transport and fate models, however, are usually obtained using sorption isotherms (Seuntjens et al., 2001; Hutchison et al., 2003; Moradi et al., 2005). This may be misleading, if sorption isotherms do not follow their corresponding desorption isotherms. This phenomenon, i.e., nonunique relationship of solution concentration

and sorbed amount of a chemical when equilibrium is reached from forward or reverse directions, is called sorption–desorption hysteresis.

Hysteresis and irreversibility have been interchangeably used in the literatures. Morton et al. (2001) described Cu sorption on montmorillonite "reversible", if desorption was complete within the time frame of sorption. Strawn and Sparks (1999) believed that "true-hysteresis" arises from a shift in the equilibrium point when a reaction approaches equilibrium from desorption direction rather than sorption. They termed the commonly observed sorption irreversibilities "pseudo-hysteresis" since such irreversibilities are generally the results of time-wise incomplete desorption experiment to reach true-equilibrium, due to the slow kinetics involved.

One possible explanation for slow desorption is that chemisorption reactions usually require a much higher activation energy in desorption direction than sorption, to break the energetically very favorable bonds of the sorbate with the surface (McBride, 2000; Appel and Ma, 2002). Morton et al. (2001) reported that Cu sorption irreversibility on montmorillonite was due to the formation of kinetically irreversible Cu dimer complexes or coordination of Cu on the high-energy edge sites of the clay.

Dissolution of the precipitated phases, developed in the sorption period, may also contribute in the slow release process, depending on the type of the precipitates and aging time. Ainsworth et al. (1994) suggested that incorporation of Cd and Co into a hydrous ferric oxide structure during recrystalization was the reason for the large desorption hysteresis. The extent of desorption irreversibility in an experiment, therefore, largely depends on the mechanisms involved in the sorption process.

Palygorskite and sepiolite are specific silicate clay minerals found in many soils of arid and semiarid regions in association with carbonates (Khademi and Mermut, 1998). Knowledge of metal sorption and desorption characteristics of heavy metals on/from these minerals is of importance in determining the fate of metals introduced to the soils through various human activities.

Several investigations have been performed to understand the sorption characteristics and mechanisms of trace elements on palygorskite, sepiolite and calcite. Alvarez-Ayuso and Garcia-Sanchez (2003a,b), for example, suggested that replacement of structural Mg at the edges of octahedral sheets and reaction of heavy metals with numerous surface silanol groups are the main mechanisms involved in heavy metals sorption on palygorskite and sepiolite. There is a lack of knowledge, however, on the desorption behavior of metals from these fibrous silicate minerals.

In case of calcite, Davis et al. (1987) proposed an initial rapid exchange of Cd^{2+} for Ca^{2+} on the surface sites and slow diffusion of the metal into the hydrated $CaCO_3$, completed within 24 h, followed by $(Cd,Ca)CO_3$ coprecipitation continued over eight days. Based on an isotopic exchange method, these researchers reported that only 12% of the Cd was reversibly sorbed on the calcite after

24 h period at pH 8, as a large amount of Cd had diffused into the calcite lattice. Martin-Garin et al. (2003), studying Cd uptake by calcite from aqueous solution using a stirred flow-through reactor experiment, demonstrated that Cd was irreversibly retained by calcite for the solution residence times more than 0.7 h.

Although sorption studies of heavy metals on soil constituents are quite numerous, those of desorption are limited. Information on the sorption reversibility of metals from soil particles, and particularly from the fibrous silicate minerals and calcite, are also very scarce. The objectives of this study were to: (i) compare sorption and desorption isotherms of Cd by palygorskite-, sepiolite-, and calcite-water systems, and (ii) find out the possible irreversibility and hysteresis phenomena of the reactions.

2. Materials and methods

2.1. Materials

Palygorskite from Florida (the Source Clay Minerals Repository, Purdue University, IN), sepiolite of Vicalvaro (TOLSA, Madrid, Spain) and calcite (BDH, Poole, UK) were used in this study. The possible carbonates, organic matter and iron/manganese oxides impurities in the clay samples were removed using acetate-buffer of pH 5, 30% H_2O_2 and citrate-bicarbonate-dithionate, respectively, according to Kittrick and Hope (1963). X-ray diffraction patterns obtained for orientated samples with a XD-610 Shimadzu X-ray Diffractometer (Cu-Kα) indicated the samples were mainly contained palygorskite, sepiolite, or calcite. The <2 μm clay fractions were then separated by centrifugation and saturated with Ca using 0.5 M $CaCl_2$ solution. Excess salts were then rinsed from the samples with deionized water until the electrical conductivity of eluents reached about 30 μS m^{-1}. The Ca-clays were then freeze-dried. The specific surface area (SSA) and cation exchange capacity (CEC) of the minerals were determined using BET-N_2 adsorption analysis and ammonium acetate method described by Rhoads (1986), respectively (Table 1).

The reagents used in this study were extra pure analytical grades: $CdCl_2 \cdot 2.5H_2O$ (BDH Chemicals, UK), and $CaCl_2 \cdot 2H_2O$, (Merck, Germany).

2.2. Cadmium sorption–desorption procedure

Prior to sorption experiments, samples of 0.3 g palygorskite or sepiolite, or 1.5 g calcite were suspended in 20 ml 0.01 M $CaCl_2$ solution in 100 ml polyethylene

Table 1
Specific surface area (BET SSA) and cation exchange capacity (CEC) of the minerals used in this research

	Palygorskite	Sepiolite	Calcite
BET SSA (m^2 g^{-1})	136 ± 4	240 ± 4	0.8 ± 0.1
CEC (cmol$_c$ kg^{-1})	19.5 ± 0.5	11 ± 0.5	–

centrifuge tubes and maintained for 24–48 h until their pH were reached to constant values. The initial pH values of the systems were 7.4 ± 0.1, 7.8 ± 0.2 and 7.5 ± 0.1 for palygorskite, sepiolite, and calcite systems, respectively.

To obtain sorption isotherms, the suspensions were treated with 10 mls of solutions containing various Cd concentrations. For each mineral, the amount of Cd introduced to the systems varied between 20% and 100% (eight levels) of its Cd maximum sorption capacity (SC_{max}). The SC_{max} of the minerals had previously been determined by Shirvani et al. (in press). The resultant initial Cd concentrations ranged from 19.5 to 97.5 $\mu mol \, l^{-1}$ for palygorskite, 92.2 to 460.8 $\mu mol \, l^{-1}$ for sepiolite and 4.7 to 23.4 $\mu mol \, l^{-1}$ for calcite. The suspensions were then shaken for 24 h at ambient temperature ($23 \pm 1 \, °C$) after addition of one drop of toluene to inhibit microbial interferences. Preliminary kinetic tests suggested that pseudo-equilibrium was reached within 24 h.

At the end of the shaking period, the suspensions were centrifuged (5000 g for 20 min) and 10 ml aliquot was pipetted out from each tube to determine Cd concentrations by an AAnalyst Perkin–Elmer 200 Atomic Absorption Spectrophotometer (AAS) at the wavelength of 228.8 nm. The detection limit of AAS for Cd determination was 0.01 mg l^{-1}. Sorption isotherms were then plotted after calculating the amount of Cd sorbed on each mineral by the difference between the initial and final concentrations of Cd in the supernatants. Visual MINTEQ (ver. 2.32) chemical equilibrium model was also used to check for possible supersaturation state in the supernatants (Gustafsson, 2005).

Immediately after sorption, desorption experiments were carried out on the systems with Cd loading of 40%, 70%, and 100% of SC_{max} by replacing the removed 10 ml equilibrium aliquots with the same volume of Cd-free 0.01 M $CaCl_2$ solutions. This process resulted in dilution of the Cd concentration in the solutions and thus perturbation of the pre-established equilibria. The systems were subsequently shaken for another 24 h, reequilibrated, centrifuged and the supernatants were analyzed to determine the new Cd distribution between the solid and solution phases. Preliminary cadmium release kinetic tests showed that pseudo-equilibrium states were established within 24 h in the systems.

The desorption cycles were repeated five times and then desorption isotherms were prepared by plotting the amounts of Cd remained in the solid phase after each desorption cycle vs. the corresponding equilibrium Cd concentrations in solution.

All Cd sorption and desorption experiments were carried out in duplicate and the average values were used for developing the isotherm.

Concentration-dependent Cd distribution coefficient (k_d) ($l \, g^{-1}$) was calculated for both sorption and desorption data:

$$k_d = \frac{q_e}{C_e} \tag{1}$$

where, q_e ($\mu mol \, g^{-1}$) is the quantity of sorbed Cd and C_e is the corresponding Cd concentration ($\mu mol \, l^{-1}$) at equilibrium. The k_d values were determined at each concentration and then averaged across all equilibrium concentrations to obtain a single estimate of distribution coefficient ($\bar{k}_d$) for the sorption and desorption isotherms.

Sorption and desorption isotherms were fitted to the Freundlich equation using the non-linear least square analysis. The Freundlich equation can be presented as

$$q = A_{sorb} C^{N_{sorb}} \tag{2}$$

$$q = A_{desorb} C^{N_{desorb}} \tag{3}$$

where, q is the quantity of Cd in solid phase $\mu mol \, g^{-1}$, C is equilibrium Cd concentration (μM), A_{sorb} and N_{sorb} are Freundlich sorption constants and A_{desorb} and N_{desorb} are Freundlich desorption constants. The goodness of fit was evaluated based on coefficients of determination (r^2) and standard errors (SE) calculated as follows:

$$SE = \left(\frac{\Sigma(q_e - q'_e)^2}{n-2} \right)^{1/2} \tag{4}$$

where, q_e and q'_e are measured and calculated amounts of Cd sorbed at equilibrium, and n is the number of measurements.

Finally, each couple of sorption and desorption isotherms was compared to check their singularity and the following indices were calculated when hysteresis observed in the sorption and desorption isotherms:

(i) Hysteresis index based on the quantity of Cd sorbed (Ma et al., 1993):

$$\omega = \frac{max(q_{desorb} - q_{sorb})}{q_{sorb}} \times 100 \tag{5}$$

(ii) Hysteresis index based on the Freundlich exponent (Turin and Bowman, 1997):

$$\eta = \frac{N_{sorb}}{N_{desorb}} \tag{6}$$

(iii) Hysteresis index based on the Cd distribution coefficient (Xiangke et al., 2000):

$$HC = \frac{\bar{k}_{d(desorb)} - \bar{k}_{d(sorb)}}{\bar{k}_{d(desorb)}} \times 100 \tag{7}$$

where, η, ω and HC are hysteresis indices, max (q_{desorb}–q_{sorb}) is the maximum difference between the sorption and desorption branches ($\mu mol \, g^{-1}$), N_{sorb} and N_{desorb} are the exponent of the fitted Freundlich equation in the sorption and desorption branches, respectively, and $\bar{k}_{d(sorb)}$ and $\bar{k}_{d(desorb)}$ ($l \, g^{-1}$) are the average apparent distribution coefficients for sorption and desorption branches, respectively.

3. Results and discussion

Cadmium sorption and desorption isotherms are shown in Fig. 1. As revealed from the desorption isotherms,
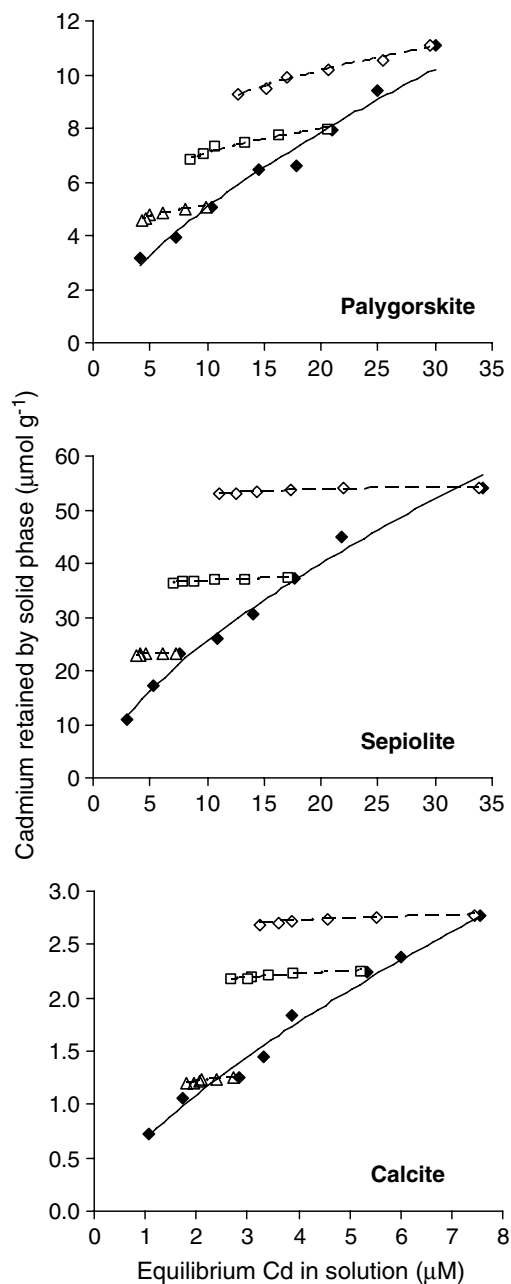
Fig. 1. Cadmium sorption isotherms (◆) and desorption isotherms at three initial Cd loads of 40% (△), 70% (□) and 100% (◇) of the mineral SC$_{max}$. Solid and dashed lines are Freundlich model predictions of sorption and desorption, respectively.

Cd concentration in the equilibrium solutions decreases significantly with a little change in the amount of Cd retained by the solid phase. The quantity of Cd desorbed from the minerals after five cycles of desorption were small, varied between 10.5% to 16.4% for palygorskite, 2.1% to 2.5% for sepiolite, and 3.0% and 4.6% for calcite, depending on the initial load of Cd on the minerals. Ainsworth et al. (1994) also reported that 53% of the Cd and 20% of Co retained by a hydrous ferric oxide did not recovered even after desorption time of 16 weeks. Filius et al. (1998) observed that hysteresis of Cd desorption

from some acidic soils still remained after 50 days of equilibration.

For a given Cd equilibrium concentration in solution, the quantity of Cd retained by each mineral was always lower based on sorption isotherms compared to their corresponding desorption isotherms, indicating that some reactions involved in the sorption processes may be irreversible or very slowly reversible. It is unlikely that substantial Cd sorption irreversibilities observed in our study are solely because of non-equilibrium state, as kinetic examinations on the same systems showed that both sorption and desorption rates of Cd significantly decreased after an initial fast process, and almost leveled within about 24 h.

Inner-sphere adsorption and nucleation processes might have caused the observed hystereses in our study, as the presence of 0.01 M Ca^{2+} in the background solutions likely inhibited the Cd outer-sphere adsorption via weak ion exchange process. Shirvani et al. (in press), working on the Cd sorption on the same minerals, suggested that Mg substitution on the edges of the clays by Cd and complexation of the metal on surface functional groups of the palygorskite and sepiolite as well as Cd precipitation on the clays and calcite surfaces were the possible mechanisms involved in Cd sorption process. Businelli et al. (2003) stated that lead desorption hysteresis by montmorillonite was due to irreversible Pb inner-sphere binding to the mineral edge sites and its precipitation at pH values higher than the hydrolysis point of Pb. Padmanabham (1983) attributed the apparent hysteresis between adsorption and desorption of Cu on goethite to the existence of low- and high-energy surface sites that provided readily- and less-readily desorbed fractions of copper, respectively.

Speciation calculations using Visual MINTEQ showed that none of the equilibrium solutions was supersaturated with respect to Cd-containing minerals (data not shown). Undersaturation state of the systems, however, does not exclude the possibility of Cd surface precipitation or coprecipitation processes. It is known that the presence of suspended colloids can trigger the nucleation of elements on the surfaces even in diluted solutions undersaturated with respect to known individual minerals in the environment (McBride, 2000).

The gap between sorption and desorption branches of the isotherms can be standardized using the ω index (Table 2). Among the minerals studied, sepiolite showed the highest ω values regardless of the Cd load on the mineral surface. Compared to the silicate clays, calcite possessed much smaller ω index at low Cd surface load, but its ω values drastically increased, and exceeded those of palygorskite, as the quantity of the Cd load increased. This is likely due to a possible shift in the Cd retention mechanism from more reversible (e.g., adsorption) to more irreversible (e.g., nucleation) processes, as the amount of Cd entered to the systems increased.

Both Cd sorption and desorption isotherms were satisfactorily described using the Freundlich equation. The model

Table 2
Hysteresis indices calculated for quantification of the nonsingularity of Cd sorption and desorption isotherms

Initial Cd load (% of the SC_{max})[a]	Hysteresis index[b]	Palygorskite	Sepiolite	Calcite
40	ω (%)	55.46	67.41	16.82
	η	5.88	9.02	6.87
	HC (%)	48.04	51.32	19.35
70	ω (%)	47.94	77.52	67.38
	η	3.72	25.02	13.72
	HC (%)	27.84	36.44	31.03
100	ω (%)	57.02	94.53	75.84
	η	3.10	34.79	19.68
	HC (%)	18.31	39.43	29.73

[a] SC_{max} = maximum sorption capacity of the minerals for Cd.

[b] $\omega = \dfrac{\max(q_{desorb} - q_{sorb})}{q_{sorb}} \times 100$, $\eta = \dfrac{N_{sorb}}{N_{desorb}}$, $HC = \dfrac{\bar{k}_{d(desorb)} - \bar{k}_{d(sorb)}}{\bar{k}_{d(desorb)}} \times 100$.

constants (A and N), coefficients of determination (r^2) and standard errors (SE) for the fitted Freundlich are presented in Tables 3 and 4, for sorption and desorption isotherms, respectively. The constant A of the Freundlich equation is a quantity parameter, i.e., the amount of Cd retained on the solid phase when the Cd concentration is one μM. The Freundlich A constants for each mineral obtained from the desorption isotherms (A_{desorb}) were significantly higher than that calculated from the sorption isotherms (A_{sorb}) (Tables 3 and 4).

The average ratio of Freundlich exponents ($\eta = N_{sorb}/N_{desorb}$) were 4.2, 22.9, and 13.4 for palygorskite, sepiolite, and calcite, respectively (Table 2). The η values greater than one indicates hysteresis as suggested by Turin and Bowman (1997). The Freundlich exponent ratios obtained in our study are distinctly greater than those reported by Seybold and Mersie (1996) and Turin and Bowman (1997) for some organic chemicals in soils, where the degree of sorption reversibilities were also much higher than those observed here for Cd sorption on the minerals.

Distribution coefficient (k_d) is defined as the ratio of an element concentration associated with the solid to the element concentration in the surrounding aqueous solution when the system is at equilibrium. For the three minerals, k_d values obtained from the sorption data generally decreased as the Cd concentration in equilibrium solution

Table 3
Estimated parameters (A_{sorb} and N_{sorb}), coefficients of determination (r^2), and standard errors (SE) for fitted Freunlich equation to the Cd sorption data

	Palygorskite	Sepiolite	Calcite
A_{sorb}	1.164 (0.124)[a]	5.690 (0.384)	0.672 (0.036)
N_{sorb}	0.638 (0.039)	0.651 (0.027)	0.698 (0.039)
r^2	0.977[***]	0.990[***]	0.982[***]
Model SE (μmol g^{-1})	0.070	0.056	0.067

[***] Significant at probability level < 0.001.

[a] Values in parentheses are standard errors associated with estimated model parameter.

Table 4
Estimated parameters (A_{desorb} and N_{desorb}), coefficients of determination (r^2), and standard errors (SE) for fitted Freundlich equation to the Cd desorption data

Initial Cd load (% of the SC_{max})[a]		Palygorskite	Sepiolite	Calcite
40	A_{desorb}	3.957 (0.133)[b]	22.118 (0.246)	1.128 (0.017)
	N_{desorb}	0.108 (0.018)	0.027 (0.007)	0.102 (0.019)
	r^2	0.897[**]	0.793[*]	0.882[**]
	Model SE (μmol g^{-1})	0.014	0.004	0.007
70	A_{desorb}	4.757 (0.208)	34.505 (0.220)	2.068 (0.028)
	N_{desorb}	0.171 (0.017)	0.026 (0.003)	0.051 (0.011)
	r^2	0.961[***]	0.959[***]	0.847[**]
	Model SE (μmol g^{-1})	0.013	0.002	0.006
100	A_{desorb}	5.463 (0.210)	50.737 (0.659)	2.589 (0.024)
	N_{desorb}	0.206 (0.013)	0.019 (0.004)	0.035 (0.006)
	r^2	0.984[***]	0.810[*]	0.892[**]
	Model SE (μmol g^{-1})	0.009	0.004	0.004

[*], [**], and [***]: significant at probability levels < 0.05, < 0.01 and < 0.001, respectively.

[a] SC_{max} = maximum sorption capacity of the minerals for Cd.

[b] Values in parentheses are standard errors of the estimated model parameters.

increased (Fig. 2). The decline in k_d values is usually attributed to saturation of adsorption sites, and is indicative of nonlinear sorption behavior, in the sorbate concentration range investigated.

Comparing the k_d values in Table 5 indicates that the affinity of Cd to the sorbents was greater in low Cd loading
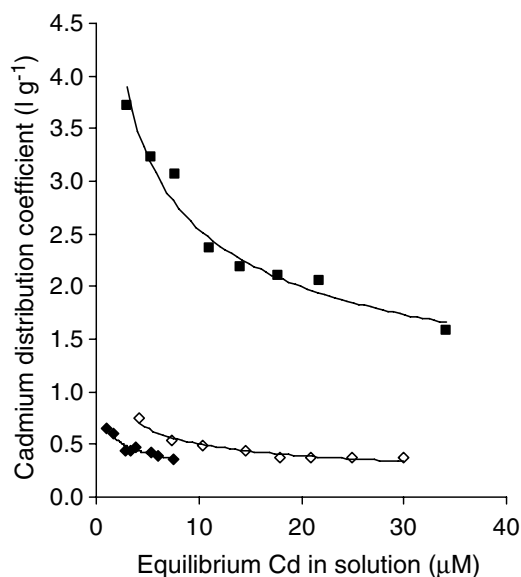

Fig. 2. Relationship between Cd distribution coefficient and equilibrium Cd concentration in palygorskite ($\diamond$), sepiolite ($\blacksquare$), and calcite ($\blacklozenge$) systems.

Table 5
Average Cd distribution coefficients ($\bar{k}_d$) obtained from sorption and desorption data

	Initial Cd load (% of the SC$_{max}$)[a]	$\bar{k}_d$ (l g^{-1})		
		Palygorskite	Sepiolite	Calcite
Sorption		0.464 (0.046)[b]	2.536 (0.254)	0.475 (0.037)
Desorption	40	0.893 (0.085)	5.214 (0.377)	0.589 (0.023)
	70	0.643 (0.057)	3.991 (0.417)	0.689 (0.039)
	100	0.568 (0.054)	3.652 (0.411)	0.676 (0.058)

[a] SC$_{max}$ = maximum sorption capacity of the minerals for Cd.
[b] Values in parentheses are standard errors associated with the estimated average Cd distribution coefficients.

systems, since k_d has been proposed as a useful parameter to assess metal-surface affinity (Atanassova, 1995; Oscarson and Hume, 1998). Cadmium may initially sorbed on high-energy (high-affinity) sites at low surface coverage and on high- and low-energy sites at higher surface coverage.

The average Cd partitioning coefficients ($\bar{k}_d$) calculated based on desorption isotherms were always greater than those calculated from the sorption isothems (Table 5), demonstrating that the affinity of Cd for the sorbents increased from the forward (sorption) to the reverse (desorption) direction. This increase of k_d, i.e. increase in the affinity of sorbate for solid phase when equilibrium is approached from desorption direction, has been defined as an indicator of hysteresis by Essington (2004).

The hysteresis coefficient (HC) values obtained based on the inconsistency of sorption and desorption $\bar{k}_d$ values are presented in Table 2. The HC trend for the minerals nearly followed those demonstrated by previous indices (ω and η). Xiangke et al. (2000) also quantified hysteresis of radiocesium sorption/desorption on a red soil using HC and argued that clay minerals and organic matter instead of iron oxides are responsible for the observed hysteresis.

4. Conclusions

Cadmium sorption and desorption isotherms on palygorskite, sepiolite, and calcite were determined using a batch method. Freundlich equation was well fitted to the obtained sorption and desorption isotherms. Desorption of Cd in 0.01 M CaCl$_2$ solution did not follow the corresponding sorption data, suggesting that Cd sorption–desorption hysteresis occurred in the systems. Several indices calculated based on the differences of the quantity of Cd sorbed, the fitted Freundlich exponent or the average Cd distribution coefficient were used to quantify hysteretic behavior observed in the systems. Small percentages of the sorbed Cd were desorbed even after applying five successive dilution cycles on the systems.

The affinity of Cd for solid phase increased from forward (sorption) to reverse (desorption) direction as the Cd partitioning coefficients calculated from desorption isotherms were higher than those obtained from corresponding sorption isotherms.

Further researches are needed to determine the cause(s) of Cd sorption–desorption hysteresis in these minerals using chemical, microscopic, and spectroscopic techniques.

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