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Tomas Undabeytia, Shlomo Nir, Giora Rytwo, Esmeralda Morillo ...+1 more authors

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MODELING ADSORPTION-DESORPTION PROCESSES OF Cd ON MONTMORILLONITE

T. UNDABEYIA,^{1,2} S. NIR,¹ G. RYTWO,^{1,3} E. MORILLO² AND C. MAQUEDA²

¹ Seagram Center for Soil and Water Sciences, Faculty of Agriculture, P.O. Box 12, Rehovot 76100, Israel

² Instituto de Recursos Naturales y Agrobiología, CSIC, Apdo 1052, Sevilla 41080, Spain

³ MIGAL, Galilee Technological Center, Kyriat Shmona, 10200, Israel

Abstract—Adsorption-desorption of Cd to Ca montmorillonite (SAz-1) was studied at concentrations ranging from 44.5 to 266.8 μM . An adsorption model was employed in the analysis of the data. The procedure consists of solving the electrostatic Gouy-Chapman equations and calculating adsorbed amounts of the cations as the sum of the cations residing in the double-layer region, and the cations chemically bound to the surface, in a closed system. The model also accounts explicitly for cation complexation in solution. The model yields good predictions for the adsorbed amounts of Cd, Ca and Mg, by employing binding coefficients from previous studies for the divalent cations and for Na, K and CdCl^+ . The model calculations also yield good predictions for the apparent hysteresis observed in the adsorbed amounts of Cd after each of 3 cycles of desorption. The apparent hysteresis is explained by the reduction in the total concentrations of Ca and Mg in desorption cycles, and the corresponding increase in the magnitude of the surface potential. Our estimates indicate that adsorption of Cd is mostly to planar, rather than edge sites of the clay mineral.

Key Words—Cadmium, Cation Adsorption Model, Hysteresis, Montmorillonite.

INTRODUCTION

Cadmium pollution in soils has increased during the last decades, mainly due to the large application of farmyard manure, sewage sludges, mining waters or fertilizers obtained from phosphorites of usually very high Cd content (Mortvedt 1987; Vanni et al. 1994).

The major factors affecting the chemistry of Cd in solution are complexation reactions, pH, ionic strength, competing ions, precipitation and the binding power to the adsorbent (Gerritse and Van Driel 1984; Christensen 1989). Cadmium sorbed on soil is strongly influenced by soil pH, cation exchange capacity (CEC) and organic content (Basta et al. 1993; Sanchez-Martin and Sanchez-Camazano 1993). However, direct cause-and-effect relationships between soil composition and metal adsorption are difficult to determine because soil components are often intercorrelated. Thus, the clay particle aggregates, as well as the clay-humic and metal-humic interactions that are usually present in soil solutions, are influenced by the ionic strength and the solution pH in a different way than in suspensions containing only the clay or the humic acid (Taylor and Theng 1995). However, good correlation has been observed between Cd adsorption on soil and their clay content (Navrot et al. 1978; Basta et al. 1993).

Estimation of the potential toxicity of Cd content in soils requires information on both the adsorption and desorption reactions. A comparison between adsorption and desorption results frequently reveals a hysteretic phenomenon. Although this apparent partial irreversibility has been described very early in the literature (Hisschemöller 1921), a satisfactory explanation

is still missing. In the case of 2:1 clay minerals, various mechanisms have been proposed: heterogeneity of sites at the surface of the exchanger; differential hydration of the exchanging cations; dehydration of the clay; crystalline swelling hysteresis; and inaccessibility of sites caused by domain or quasi-crystal formation (Maes and Cremers 1975; Kool and Parker 1987; Verbug and Baveye 1994). In this article, results of Cd adsorption on and desorption from montmorillonite are presented, and it is shown that both can be explained consistently by the application of a general model for cation adsorption in a closed system (Nir 1984, 1986), which was further developed for Cd adsorption by explicitly accounting for Cd complexation in solution (Hirsch et al. 1989).

MATERIALS AND METHODS

Experimental

The clay used was a standard montmorillonite from Arizona (SAz-1 montmorillonite, van Olphen and Fripiat 1979) supplied by the Clay Minerals Society, without further treatment. Its CEC was determined to be 123.5 meq/100 g, of which 100.78 meq corresponded to Ca, 19.16 meq to Mg, 2.6 meq to Na and 0.96 meq to K.

The adsorption experiments were done in triplicate in 50-mL polypropylene centrifuge tubes, by mixing 0.1 g of clay mineral with 20 mL of solutions containing various concentrations of Cd. The concentrations used were 44.5, 89.0, 133.5, 177.9, 222.5 and 266.9 μM . All experiments were carried out in 0.01 *N* NaCl medium to keep the ionic strength constant. The

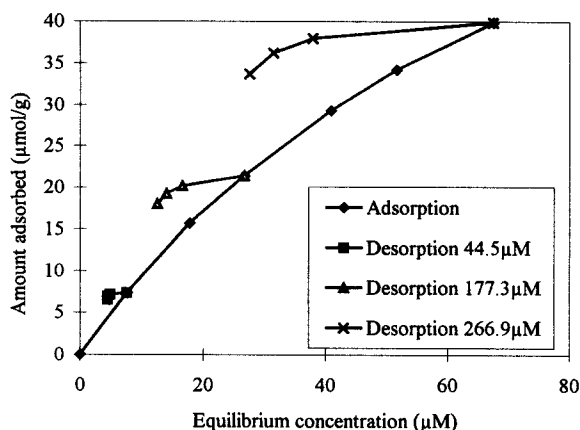


Figure 1. Adsorption-desorption isotherms of Cd on montmorillonite. The relative standard deviations were 3%. Experimental values. Calculated values are given in Tables 1 and 2.

samples were shaken for 24 h at 20 ± 1 °C. The concentrations of Cd, Ca and Mg in solution were determined by atomic absorption spectrometry and K by flame photometry. The amounts of adsorbed Cd were determined from the difference between the concentrations before and after reaching equilibrium.

The desorption experiments were performed after equilibrium in adsorption was reached, by removing half of the supernatant after centrifugation, which was replaced by 10 mL of 0.01 N NaCl. This process was repeated twice more. The equilibrium pH for both adsorption and desorption processes was 6.5 ± 0.2 .

Model Calculations

Model calculations followed the same procedure described by Nir (1984, 1986) and Hirsch et al. (1989). The 3 main elements in this model are 1) the adsorbed cations consist of (a) cations tightly bound to the surface (specific binding) and (b) cations residing in the double layer region; 2) the electrostatic Gouy-Chapman equations are solved for a solid/liquid system containing several cations of various valences, and particles whose surfaces are charged and partially neutralized by cation binding; and 3) the concentration of surface sites in the solid/liquid system is explicitly included in the computation, thus accounting for the concentrations of cations in solution during adsorption/desorption processes.

Let X_i^+ denote a monovalent cation that binds to singly charged negative sites, P^- , on the surface of the silicate:



The binding coefficient for such reaction, K_i , is,

$$K_i = [PX_i]/([P^-][X_i(0)^+]) \quad [2]$$

in which $[X_i(0)^+]$ is the concentration of the cation at

the surface. Divalent cations can form a 1:1 charged complex with a binding coefficient K_{j1} and a 2:1 neutral complex with a binding coefficient K_{j2} .

The 1:1 complexation is described by:



$$K_{j1} = [PX_i^+]/([P^-][X_i(0)^{++}]) \quad [4]$$

For the 2:1 complexation, we formally define a divalent site, P^{--} . The concentration of such sites is $[P^-]/2$.



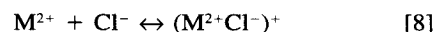
$$K_{j2} = [PX_i]/([P^{--}][X_i(0)^{++}]) \\ = [PX_i]/([P^-]/2[X_i(0)^{++}]) \quad [6]$$

In Equations [2], [4] and [6], the concentration of the cations close to the silicate layer is needed. It is calculated by the relation:

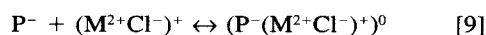
$$X_i(0) = X_i Y(0)^{z(i)}, \quad [7]$$

where $Y(0) = \exp(-e\Psi(0)/kT)$, e is the absolute magnitude of an electronic charge, $z(i)$ is the valence of the given ion, $\Psi(0)$ is the surface potential, k is the Boltzmann's factor, T is the absolute temperature and X_i is the molar concentration of cation i in its monomeric form in the equilibrium solution, far away from the surface. For a negatively charged surface, $Y(0) > 1$, and the concentration of the cation at the surface, $X_i(0)$, may be significantly larger than X_i .

In our calculations, only the 2:1 complexes were considered for the divalent cations. However, solution speciation of divalent cations, e.g.:



and adsorption to the clay of the type:



were explicitly considered as in Hirsch et al. (1989) and Rytwo et al. (1996).

RESULTS AND DISCUSSION

The adsorption of Cd on montmorillonite is plotted in Figure 1. The clay shows a higher preference for Cd at lower concentrations. This can be inferred from Table 1, in which this statement is expressed by the percentage of experimental Cd adsorbed, that is slightly reduced from 82.9% at an initial Cd concentration of 44.5 μM, to 74.7% at 266.9 μM. A similar reduction in the percentage of Ca and Mg that remains adsorbed was also observed. The calculated fraction of K adsorbed ranged from 22.4% at the lowest Cd concentration to 20.5% at the highest Cd concentration.

The results were analyzed with the adsorption model (Nir 1986; Nir et al. 1986; Hirsch et al. 1989; Rytwo et al. 1996) by using binding coefficients from previous studies (given in Table 1). The calculations con-

Table 1. Calculated surface potentials ($-\psi_0$) and percentages of Cd, Ca and Mg adsorbed on montmorillonite as a function of the amount of Cd added. Experimental and calculated values.†‡

Cd added (μM)	Cd(%)		Ca(%)		Mg(%)		$-\psi_0$ (mV)
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	
44.5	82.9	80.1	87.2	81.3	83.9	79.0	80.8
89.0	80.0	79.4	86.1	80.6	83.5	78.2	80.3
133.5	80.0	78.7	85.1	79.9	81.6	77.5	79.7
177.9	77.0	78.0	84.4	79.2	81.6	76.8	79.2
222.5	76.8	77.3	83.9	78.5	80.7	76.1	78.7
266.9	74.7	76.6	83.2	77.9	80.2	75.4	78.2

† The calculations employed the following values of binding coefficients: Ca ($6 M^{-1}$), Mg ($5 M^{-1}$) (Rytwo et al. 1996 and the current work); Cd ($10 M^{-1}$) and CdCl^+ ($30 M^{-1}$) as in Hirsch et al. (1989); Na ($0.5 M^{-1}$), K ($4 M^{-1}$) as in Nir et al. (1986). The total concentrations in the system (clay + solution) were 2.52 mM for Ca, 0.479 mM for Mg, 0.048 mM for K and 10.13 mM for Na.

‡ The relative standard deviations obtained for Cd adsorption were 3%.

sidered speciation of Cd in solution, that is, CdCl^+ and CdCl_2^0 , and also the possibility that a fraction of the Ca and Mg exists in solution as CaCl^+ and MgCl^+ (Sposito et al. 1983; Rytwo et al. 1996), but the effect of such speciation was insignificant in our case and could be ignored.

It should be emphasized that the calculated values of the amounts of cations adsorbed in a system including Cd, CdCl^+ , Ca, Mg, Na and K, are essentially predicted values, since the binding coefficients were taken from previous studies. The binding coefficients of Na and Ca, and Mg, were slightly varied in the current paper within the range of values given in Nir et al. (1986) and Rytwo et al. (1996), respectively. The results in Figure 1 and Table 1 demonstrate that the predictions are reasonably good for all the measured adsorbed amounts, especially for Cd, with differences of less than 2.8%. The last column in Table 1 gives

the calculated values of the surface potentials, which show a very slight reduction in relation to a 6-fold increase in total Cd concentrations, since its contribution to the total ionic strength was relatively small.

It is remarkable that the same binding coefficients that explained Cd adsorption at total concentrations of 1 μM (Hirsch et al. 1989) could be employed for 2 orders of magnitude larger Cd concentrations, and for a different montmorillonite clay than that previously employed, indicating that the model employed is suitable for a wide range of conditions.

The results in Figure 1 exhibit an apparent hysteresis in the desorption of Cd, that is, more Cd remains adsorbed following desorption cycles than expected. However, a comparison of the calculated values with the experimental values in Table 2 demonstrates that the model calculations yield good predictions for the remaining adsorbed amounts of Cd (as well as Ca and Mg), for all the desorption cycles (K data have not been included in the Table due to its negligible influence as discussed previously). The explanation of this hysteresis, which was in fact predicted by Nir (1986), is straightforward. The desorption cycles involve centrifugation, removal of half of the volume of the supernatant and addition of a corresponding volume of 10 mM NaCl 0.01 N, and thus the total Ca and Mg concentrations in suspension are reduced. The reduction in the concentrations of the main cations (Ca and Mg) interfering with Cd desorption results in an enhanced Cd adsorption in the desorption cycles. A small increase in the magnitude of the surface potential, due to a smaller sum of total concentrations of divalent cations, also contributes to enhanced adsorption of Cd in desorption cycles.

The heterogeneity in the distribution of the surface charge sites has been considered as a possible explanation for the hysteresis observed in the adsorption of cations on clays (Fripiat et al. 1965; Maes and Cremers 1975). According to this point of view, Cd de-

Table 2. Percentages of Cd, Ca and Mg adsorbed as a function of the amount of Cd added for the adsorption and its consecutive desorption processes. Experimental and calculated values.†

Cd added (μM)	Step†	Cd(%)		Ca(%)		Mg(%)		$-\psi_0$ (mV)
		Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	
44.5	Adsorption	82.9	80.1	87.2	81.3	83.9	79.0	80.8
	Desorption #1	87.9	83.9	90.5	84.9	87.2	83.0	84.1
	Desorption #2	88.2	86.1	92.0	87.1	89.5	85.4	86.4
	Desorption #3	88.3	87.8	93.5	88.8	89.6	87.2	88.3
133.5	Adsorption	80.0	78.7	85.1	79.9	81.6	77.5	79.7
	Desorption #1	85.9	82.9	89.8	84.0	87.5	82.1	83.3
	Desorption #2	87.3	85.4	91.7	86.4	90.1	84.7	85.6
	Desorption #3	87.6	88.0	93.1	89.0	90.7	87.5	88.6
266.9	Adsorption	74.7	76.6	83.2	77.9	80.2	75.4	78.2
	Desorption #1	83.7	81.7	89.4	82.8	86.7	80.7	82.2
	Desorption #2	85.1	84.3	90.6	85.4	88.4	83.6	84.6
	Desorption #3	85.6	86.4	92.4	87.5	90.2	85.9	86.8

† See Table 1 for the binding coefficients used in the model calculations.

Table 3. Calculated distribution of surface complexes and Cd speciation in solution as a function of its total concentration. †

Total Cd (μM)	Percentages					
	Bound as		In double layer Cd and CdCl ⁺	In equilibrium solution		
	Cd	CdCl ⁺		Cd	CdCl ⁺	CdCl ₂ ⁰
44.5	55.9	15.0	9.1	9.9	9.6	0.4
89.0	55.2	15.2	9.1	10.2	9.9	0.4
133.5	54.3	15.4	9.0	10.5	10.3	0.5
177.9	53.5	15.5	9.0	10.8	10.7	0.5
222.5	52.7	15.7	8.9	11.1	11.1	0.5
266.9	51.9	15.9	8.9	11.4	11.5	0.5

† See Table 1 for the binding coefficients used in the model calculations.

sorption would be significantly reduced from the sites with higher affinity. Verbug and Baveye (1994) pointed out that this explanation fails to consider the dynamic nature of the exchange of cations at the molecular level. According to them, the reactions of the heavy metals on the edge sites should be considered reversible. Indirect experimental evidence supporting this fact was reported by Comans (1987), who observed complete reversibility for the adsorption-desorption of Cd to illite, where the importance of the edge sites was also emphasized. Consequently, the presence of sites of different affinity on the clay, that could be related to different kinetics, should not be the origin of the above hysteresis. Verbug and Baveye (1994) tried to explain the hysteresis by a model based on 2-stage kinetics related to the adsorption on the outer surface of quasi-crystals that are broken up into smaller crystals. Although this model could explain the hysteresis qualitatively, experimental support for the model was not available. The success of our model to explain the data is based on a thermodynamic approach, by considering the electrostatic nature of the interface between the clay surface and the solution containing the different cations. Our treatment avoided consideration of the kinetics of the reactions involved. Our treatment implies that the apparent hysteresis was not due to the kinetics of Cd adsorption-desorption but rather resulted from changes in Ca and Mg solution concentrations.

Tables 3 and 4 provide details of the calculated amounts of Cd adsorbed as a divalent cation, or as the monovalent cation CdCl⁺, as well as its solution speciation. Despite the similar solution concentrations of Cd and CdCl⁺, and the higher binding coefficient of CdCl⁺ (30 M^{-1}) than that of Cd (10 M^{-1}), only about 15% of the adsorbed amount of Cd is due to adsorption as CdCl⁺. Moreover, CdCl⁺ tends to be desorbed from the clay to a larger extent than Cd. This difference is due to enhanced concentration of the divalent cation at the clay surface according to $\exp(-2e\Psi_0/kT)$

Table 4. Calculated distribution of surface complexes and Cd speciation in solution after 3 consecutive desorptions. †

Total initial Cd (μM)	Percentage					
	Bound as		In double layer Cd and CdCl ⁺	In equilibrium solution		
	Cd	CdCl ⁺		Cd	CdCl ⁺	CdCl ₂ ⁰
44.5	65.9	12.5	9.5	6.2	5.7	0.2
133.5	66.1	12.4	9.5	6.1	5.6	0.2
266.9	63.8	13.1	9.5	6.8	6.5	0.3

† See Table 1 for the binding coefficient used in the model calculations.

(see Equation [7]), which is the square of the corresponding factor for the monovalent cations. Hirsch et al. (1989) observed that more Cd was adsorbed as a monovalent than a divalent cation in a suspension containing 50 mM NaCl; under this condition the solution included several-fold more CdCl⁺ than Cd.

The adsorption of Cd on the clay is expected to occur by interchange with the cations saturating the planar positions as well as adsorption to the edge sites. Several authors (Inskeep and Baham 1983; Garcia-Miragaya et al. 1986; Morillo and Maqueda 1992) have suggested that the adsorption of heavy metals on layer silicates takes place onto sites of different affinities, filling the higher-affinity sites at lower metal coverage. Madrid et al. (1991) observed that the number of high-preference sites for heavy metal adsorption increased with the pH, and suggested that they are located in variable charge regions. Stadler and Schindler (1993) suggested that the sorption of heavy metals on the edge sites at the pH of our system (6.5) is mostly due to the aluminol sites. Zachara and McKinley (1993) reported a value of $10^{3.42}$ for the binding coefficient describing Cd adsorption on aluminol sites. Employing this binding coefficient would give complete saturation of the edge sites even in the case of the lowest Cd concentration in our system. However, the use of this binding coefficient may be limited because of the inherent difficulties in estimating the concentration of edge sites that was used in the determination of this binding coefficient.

In order to further investigate the possibility of Cd adsorption on the edge sites, Cd adsorption for the 2 lowest concentrations (44.5 and 89.0 μM) was determined for different clay concentrations. At higher clay concentrations, the importance of edge sites will be greater for the same heavy metal concentration and it would be expected that the predictions of the model which considered adsorption just to 1 type of sites would yield underestimates to the experimental results of Cd adsorption. At lower clay concentrations, the relative contribution of the edge sites to Cd adsorption would be lesser since they might constitute a smaller fraction of the total adsorbed Cd, even if fully satu-

Table 5. Cd adsorption on montmorillonite as a function of the clay concentration used. Experimental and calculated values.

Initial Cd (μM)	Clay concentration (g/L)	Theoretical percentage adsorbed	Experimental percentage adsorbed
44.5	1	65.1	61.3
	5	80.1	82.9
	7	82.6	90.2
89.0	1	62.3	56.8
	5	79.4	80.0
	7	82.0	84.6

rated. Table 5 shows Cd adsorption for several clay concentrations. Undabeytia et al. (1996) observed, by Cd adsorption to Li⁺-fixed montmorillonite, that the maximum Cd adsorption at pH 6.5 was about 20.4 $\mu\text{mol/g}$ for a solid/solution ratio of 5 g/L. The Li⁺-fixed montmorillonite eliminates almost completely the contribution of the interlayer sites in relation to adsorption due to the Hoffmann-Klemen effect (Trillo et al. 1993; Alvero et al. 1994), and hence cation adsorption results mainly on edges (Ziper et al. 1988). According to the previous value, for the lowest Cd concentration in our experiment (44.5 μM), maximum Cd adsorption on the edge sites at the lowest clay concentration would amount to about half of total Cd, whereas with 7 g/L, the edge sites would be sufficient for the adsorption of total amount of Cd.

The results in Table 5 do indicate that the calculated adsorbed amounts of Cd underestimate the experimental values for higher clay concentrations, but the deviations are only 3 to 8%. Furthermore, we employed the same binding coefficients for Cd and CdCl⁺ as in Hirsch et al. (1989), where the total concentrations of Cd varied from 0.1 to 1 μM , that is, 2 or 3 orders of magnitude below those employed in the current study. An analysis of the kinetics and equilibrium of binding of particles to 2 types of sites shows that, in general, adsorption to the more abundant low affinity sites starts before the high-affinity sites are fully saturated (Nir et al. 1994; Undabeytia et al. 1996).

In conclusion, although the model did not provide estimates for the fraction of Cd adsorbed to the edge sites, the evidence points out that, in our case, most of Cd adsorption occurs to the planar sites.

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