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RETENTION MECHANISMS OF Cd ON ILLITE

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Abstract—The adsorption of metals by clay minerals is a complex process involving different mechanisms, and is controlled by different variables which can interact. The aim of this work was to study the retention mechanisms of Cd on illite. We obtained Cd adsorption isotherms at constant pH, adsorption edges as a function of pH, adsorption isotherms at 5, 25 and 45°C (pH = 7), and response surfaces of the simultaneous effect of pH, initial concentration, ionic strength, and temperature on the retention of Cd on illite. Below pH 6, adsorption of Cd on illite is via ion exchange with H_3O^+ and Na^+ ions which saturate the exchange sites, the exchange with Na^+ being the main mechanism between pH 4.5 and 6.0. For pH values >6, the effect of ionic strength on the amount of Cd^{2+} retained decreased with pH, being negligible at pH 8; the proton stoichiometry was greater than for pH values <6 and an increase in the temperature favored the retention of Cd. These facts are compatible with a more specific process involving hydrolyzed species, in which Cd can associate with illite as an inner sphere complex.

Key Words—Cadmium, Cation Exchange, Freundlich, Illite, Langmuir, Response Surface Methodology, Retention Mechanisms, Specific Adsorption, Thermodynamic Parameters.

INTRODUCTION

Adsorption of metal ions onto mineral substrates is a critical process in soil chemistry, hydrometallurgy, and the treatment of industrial wastes. Processes as diverse as the uptake of trace nutrients by plants and the removal of toxic heavy metals from industrial wastes often depend on adsorption to mineral systems. Adsorption is a complex process, often involving much more than simple ion exchange on the mineral surface. Factors such as the pH, the nature and concentration of the substrate and adsorbing ion, ionic strength, and the presence of competing and complexing ions all affect the amount of metal ion that will adsorb (Ikhsan *et al.*, 1999). Natural systems are characterized by the presence of a wide range of metal ions in different concentration ratios, at different pH values, and with different concentrations of heterogeneous binding ligands present.

The retention of Cd by soils and related materials has been studied widely. Adsorption to clay minerals was found to be the operating mechanism at low Cd concentrations (Garcia-Miragaya *et al.*, 1986). In addition to adsorption, precipitation can play a key role in controlling Cd levels in soil, as found by Santillan-Medrano and Jurinak (1975). Several factors influence the degree to which Cd is adsorbed: pH, ionic strength, equilibrium concentration, exchangeable cations and type of ligands (Naidu *et al.*, 1997). Most of these studies used the 'one variable at a time' strategy that tacitly assumes that the variables are independent. Usually this is not true, and in these cases it is necessary to consider several factors simultaneously.

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Response surface methodology (RSM) consists of a group of mathematical and statistical techniques that are useful in the modeling and analysis of problems in which a response of interest, such as amount of metal adsorbed, is influenced by several variables. Some attractive features of RSM are that: (1) it is applicable for any number of variables; and (2) it casts the experimental problem in readily understood geometric terms (Box *et al.*, 1978). Several mathematical models could be chosen; but multilinear models are preferred to exponential models because regression methods are better established and more robust. A simple quadratic model for N input variables (Allus *et al.*, 1988) can be given by

$$y \supset b_o \quad \sum_{i\supset 1}^{i\supset N} b_i x_i \quad \sum_{i\supset 1}^{i\supset N} b_{ii} x_i^2 \quad \sum_{i\supset 2;j\supset 1}^{i\supset N,j<i} b_{ij} x_i x_j \qquad (1)$$

where y is the response (*e.g.* the amount adsorbed) and x_i is the input variable i, the term b_o is a constant corresponding to the central point of experimental variables, the terms in b_i and b_{ii} determine the influence of linear and quadratic terms of variable i on the response, whereas the cross-product terms, b_{ij}, relate to the interaction between different variables. Fitting and analyzing response surfaces is greatly facilitated by the proper choice of an experimental design.

The aim of this work was to study the retention mechanisms of Cd on illite. The specific goals were to: (1) obtain adsorption isotherms at constant pH, and by interpolation to determine the adsorption edges; (2) draw the response surface of the amount of Cd adsorbed on illite as a function of pH, ionic strength, initial concentration, and temperature; and (3) deduce the thermodynamic parameters at pH 7.

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MATERIALS AND METHODS

Illite conditioning

The illite sample was supplied by the company Socodis S.A. (Villefranche-Sur-Saône, France). The sample was ground and sieved to obtain aggregates <0.2 mm. Its mineralogical composition was illite, 90%; calcite, 7–8%; and kaolinite, 0.2%. Table 1 presents the chemical analysis of the sample (data from the supplier). To remove carbonates, 50 g of illite were treated with 100 mL of a pH 5 buffer solution made of 1 M sodium acetate and acetic acid. The suspension was stirred for 24 h, adjusting the pH to 5 when necessary. The suspension was centrifuged at 9000 × g for 30 min (Hermle, mod. Z320, Gosheim, Germany), the residue was washed twice with 0.01 M $NaNO_3$, centrifuging the suspensions after washing, at 9000 × g. Then, the illite was kept in 0.01 M $NaNO_3$ for 24 h to saturate the solid phase with Na^+. The suspension was centrifuged at 9000 × g for a further 30 min; the residue was dried at 100°C for 24 h, ground, and sieved to obtain aggregates <0.2 mm. The Fe(III) test to confirm the presence of acetate ions in the decarbonated sample was negative (Burriel *et al*., 1999). The illite pH measured in 0.01 M $NaNO_3$ was 6.5 (0.250 g of solid and 25 mL of solution). The BET surface area, measured on a Micromeritics ASAP 2010, was 141 $m^2\ g^{-1}$.

The zeta potential of an illite suspension in 0.01 M $NaNO_3$ was determined at various pH by microelectrophoresis, *i.e.* the application of dynamic light scattering (DLS) to the measurement of electrophoretic mobility (Muller, 1996). Samples of 0.2500±0.0003 g of the pretreated illite were placed in 50 mL capped polyethylene centrifuge tubes, and 24 mL of distilled water and 1 mL of 0.25 M $NaNO_3$ solution were added. The pH was adjusted by adding 0.1 M HNO_3 or 0.1 M NaOH. Suspensions were placed for 24 h in a thermostatically controlled water bath, Grant mod. SS40-2 (Grant Instrument, Cambridge, UK), coupled with a cold unit mod. C525, at 25.0±0.2°C. The pH was measured and readjusted after 3, 9 and 20 h. The total volume changes in the solution following pH readjustment ranged from 0.052 mL (0.2 vol.%) for pH 6 and 7, to 0.35 mL (1.4 vol.%) for pH 2.5. After 24 h, the equilibrium pH was measured, and the suspensions were centrifuged at 9000 × g for 5 min. Sub-samples of the supernatant liquids were injected directly into a Malvern Zetasizer 3000 instrument (Malvern Instruments, Malvern, UK).

Adsorption isotherms

Constant-pH isotherms were obtained in the pH range 2.5–8. The adsorption experiments were performed at seven total Cd concentrations equivalent to 5, 10, 25, 50, 100, 200 and 300 mmol Cd kg^{-1} illite, in an aqueous solution of 0.01 M $NaNO_3$, and at a temperature of 25,0±0.2°C. For each isotherm point, 0.2500±0.0003 g of the pretreated illite were placed in 50 mL polyethylene centrifuge tubes, and enough distilled water was added in order to have a final volume of 25 mL, 1 mL of 0.25 M $NaNO_3$, and the corresponding volume of a 1000 mg L^{-1} $Cd(NO_3)_2$ solution (Merck, Darmstadt, Germany) to obtain the desired total concentration of Cd. The pH was adjusted by adding 0.1 M HNO_3 or 0.1 M NaOH. Suspensions were equilibrated, pH adjusted, and centrifuged as described previously. After filtering the suspensions (Xinhua paper mill 102), supernatant liquids were acidified with 20 µL of HNO_3 (65%) for sample preservation, and stored for subsequent analysis. Cadmium concentrations in the supernatant liquids were analyzed by flame atomic absorption spectrometry, Perkin-Elmer mod. 2100 (Perkin-Elmer, Überlingen, Germany). The wavelength was 326.3 nm which allowed the measurement of Cd concentrations in the range 0–250 mg L^{-1} without diluting the solutions. The flow rate was 3.0 L min^{-1} for air and 1.0 for acetylene.

The adsorption edges were obtained by reading the amount adsorbed and the equilibrium concentration from the constant-pH experiment data. A blank was obtained by preparing eight 1 mM Cd solutions, equivalent to 100 mmol kg^{-1} illite, on the background electrolyte without the presence of illite; the pH of each one was adjusted to cover the pH range 2–9. The experiments were performed according to the procedure explained previously.

Simultaneous effect of pH, initial concentration, ionic strength and temperature on the retention of Cd on illite

The retention processes are controlled by different variables that can interact. One experimental approach is

Table 1. Chemical analyses of illite.

Major components (%)		Trace elements (mg kg^{-1})		Others (%)	
SiO_2	48.2	Ba	250	Carbonates	4.0
Al_2O_3	25.0	Pb	26	H_2O	12.4
K_2O	7.2	Hg	14	Structural H_2O	2.5
CaO	7.2	Cd	0.3		
Fe_2O_3	6.7	As	<0.005		
MgO	3.5				
Na_2O	1.2				
TiO_2	0.8				

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to apply the RSM for modeling the amount adsorbed as a function of the chosen variables. We used a second-order, orthogonal and rotable design, with three levels for each factor. The first level comprises the central points, coded as 0, which are also used to obtain the system experimental error; the second level are the points of the first-order design, coded as 1 and −1; and the third level includes the second order or axial points that are coded as α and $-\alpha$, where α is the number of first-order points raised to the power of 1/4. Axial points allow the adjustment of the curvature of the response. An orthogonal experiment minimizes the regression coefficients variance. The rotability reflects the fact that the variance of the response is a function of the distance of the experimental point to the central point, but not of the direction; therefore, the variance will not change by rotating around the central point. Rotability is a very useful property of a response surface because we do not initially know its shape.

Statgraphics software version V4.1 (Manugistics, 1998) was used to obtain the combination of values that draw the surface response within the region of the four-dimensional observations space. The model evaluates the effect of each independent variable and their interactions on the amount of Cd adsorbed on illite. Two sets of experiments were designed differing in the pH range. In the first experiment the pH varied between 2.7 and 7.9; the second experiment was restricted to the range 6–8, where pH had a more marked effect on the amount of Cd adsorbed. Table 2 includes the actual design with coded values of the variables, and Table 3 presents the coded and actual values of the variables for the two different pH range experiments. In both experiments the runs were randomized.

For each run, 0.2500±0.0003 g of the pretreated illite were placed in 50 mL polyethylene centrifuge tubes, and enough distilled water was added in order to have a final volume of 25 mL, the corresponding volume of a 4 M or 0.25 M $NaNO_3$ solution to adjust the ionic strength, and the volume of a 1000 mg L^{-1} $Cd(NO_3)_2$ solution (Merck, Darmstad, Germany) to obtain the desired total concentration of Cd. The pH was adjusted by adding 0.1 M HNO_3 or 0.1 M NaOH. Suspensions were equilibrated, centrifuged, and the supernatant liquids were analyzed in the same way as described before.

Table 2. Second-order, rotable and orthogonal central composite experimental design with codified variables for four variables and one response.

Run	pH	Temperature	log [$NaNO_3$]	Cd initial concentration
1–12	0	0	0	0
13	−1	−1	−1	−1
14	1	−1	−1	−1
15	−1	1	−1	−1
16	1	1	−1	−1
17	−1	−1	1	−1
18	1	−1	1	−1
19	−1	1	1	−1
20	1	1	1	−1
21	−1	−1	−1	1
22	1	−1	−1	1
23	−1	1	−1	1
24	1	1	−1	1
25	−1	−1	1	1
26	1	−1	1	1
27	−1	1	1	1
28	1	1	1	1
29	−2	0	0	0
30	2	0	0	0
31	0	−2	0	0
32	0	2	0	0
33	0	0	−2	0
34	0	0	2	0
35	0	0	0	−2
36	0	0	0	2

Thermodynamic parameters were estimated from the temperature dependence of the Langmuir constant (Angove *et al.*, 1998) obtained from Cd adsorption isotherms (pH 7) at 5, 25 and 45°C following the experimental procedure described above. According to the response surface results, temperature significantly affected Cd retention on illite from pH 6 to 8. We chose pH 7 because that was an intermediate point in the section where pH had the largest effect on the amount of Cd adsorbed.

Table 3. Coded and actual values for the experiments described in the text.

	Coded value	pH	Temperature (°C)	log [$NaNO_3$]	Cd initial concentration (mmol kg^{-1})
Experiment A	−2	2.7	5.0	−3.5	10
	−1	4.0	15.0	−2.5	80
	0	5.3	25.0	−1.5	150
	1	6.6	35.0	−0.5	220
	2	7.9	45.0	0.5	290
Experiment B	−2	6.0	5.0	−3.5	10
	−1	6.5	15.0	−2.5	80
	0	7.0	25.0	−1.5	150
	1	7.5	35.0	−0.5	220
	2	8.0	45.0	0.5	290

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RESULTS AND DISCUSSION

Adsorption isotherms at constant pH

Figure 1 contains the adsorption isotherms of Cd on illite at constant pH, 25°C, and 0.01 M concentration of $NaNO_3$. Each isotherm represents the variation of the amount of Cd adsorbed on illite (n^a), expressed in mmol kg^{-1}, against the solution Cd concentration, expressed in mM. The initial slope and the amount of Cd adsorbed increased with pH. According to the Giles classification (Giles *et al.*, 1960; Hinz, 2001), the adsorption isotherm at pH 2.5 was S-3 type, characterized by a gentle initial slope that reached a short plateau before increasing the amount adsorbed when the Cd equilibrium concentration in solution increased. This shape suggests that at pH 2.5 and low equilibrium concentrations, the affinity of the illite for Cd was smaller than the affinity of that clay mineral for cations in 0.01 M solution (H_3O^+, Na^+, Al^{3+}). At acidic pH, protonation of surface active sites as well as competition of H_3O^+ and dissolved Al^{3+} for exchange sites increases.

Adsorption isotherms at pH 4, 5, 6 and 7 were L-2 type, characterized by a steep initial slope that levels off as the equilibrium concentration of metal increases, giving rise to a linear section of positive slope. These features indicate that the affinity of illite for Cd^{2+} decreases as the covering increases. The curves obtained at pH 4, 5 and 6 had similar segments above the isotherm inflexions which suggest that the number of active sites scarcely varied in that pH range. The pH 7 isotherm had a sharper slope than the previous isotherms that could be attributed to the variation of the acid-base properties of the illite surface. Probably, it increased the number of negative active sites due to the dissociation of H-containing functional groups. The adsorption isotherm at pH 8 was of H-1 type, and it showed an abrupt initial part in which almost all Cd initially added was adsorbed. This type of isotherm is associated with the retention of hydrolyzed metallic ions (Tiller *et al.*, 1979; Naidu *et al.*, 1994) and, in general, reflects a high affinity adsorbent-adsorbate.

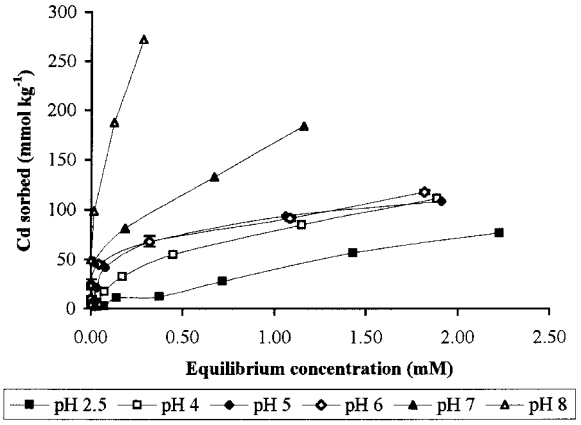


Figure 1. Constant-pH adsorption isotherms of Cd on illite at 25°C and 0.01 M $NaNO_3$. Confidence intervals for the pH 6 isotherm are included.

Several authors (Cavallaro *et al.*, 1978; Tiller *et al.*, 1984; Bolton *et al.*, 1996; Pardo, 1997; Echeverría *et al.*, 1998; Morera *et al.*, 2001) have obtained adsorption isotherms in different adsorbents similar to those included in Figure 1. Angove *et al.* (1997) reported two isotherms of Cd on kaolinite at pH 5.5 and 7.5, both of which were of L-2 type and the adsorption increased with pH. They concluded that at pH 5.5, adsorption takes place on the sites of negative permanent charge of the siloxanic layer, and the retention is due to electrostatic forces; whereas at pH 7.5, adsorption was stronger and occurred on the variable charge sites of the kaolinite.

Traditionally, the adsorption of ions by clay minerals and soils has been described quantitatively by parameters obtained using Langmuir and Freundlich models. Figure 2a shows the variation of the n_m^a and B_L parameters with pH. We did not include the values corresponding to pH 2.5 isotherms because they were S type. The monolayer capacity decreased slightly between pH 4 and 6, and then it increased to 350 mmol kg^{-1}. The Langmuir bonding term, B_L, increased with pH, indicating that the interaction energies increased with pH.

The Freundlich model is an extension of the Langmuir model to an heterogenous surface (Elkhatib *et al.*, 1991). Figure 2b shows the effect of pH on these two parameters. The Freundlich distribution coefficient scarcely varied for pH values between 4 and 6, and increased for pH values >6. The magnitude of n decreased in the pH range 4–6 from 0.8 to 0.24, indicating that the inflection of the isotherms was becoming more acute; from pH 6 it increased gently to 0.35 at pH 8.

Adsorption edges

Figure 3 illustrates the relationship between the amount adsorbed and pH for different initial concentrations of Cd. These plots were obtained from the experimental results obtained at constant pH. It includes a curve corresponding to a 1 mM Cd(II) solution without illite, equivalent to an initial concentration of 100 mmol kg^{-1} illite, that was used as a blank. For initial concentrations of Cd equivalent to 5 and 10 mmol kg^{-1}, the illite retained all the Cd added in the whole pH range studied; therefore, the amount adsorbed was independent of pH. For initial concentrations of 25 and 50 mmol kg^{-1}, the amount adsorbed was proportional to pH from pH 2.5 to 4, where retention equalled 100% of the initial Cd. For larger initial concentration of Cd (100, 200 and 300 mmol kg^{-1}), three sections were observed. From pH 2.5 to 4, the amount adsorbed increased linearly with pH, and the slopes were parallel. In the second section, between pH 4 and 6, the amount adsorbed was independent of pH. In the third section, which includes pH 6 and 8, the amount adsorbed and the

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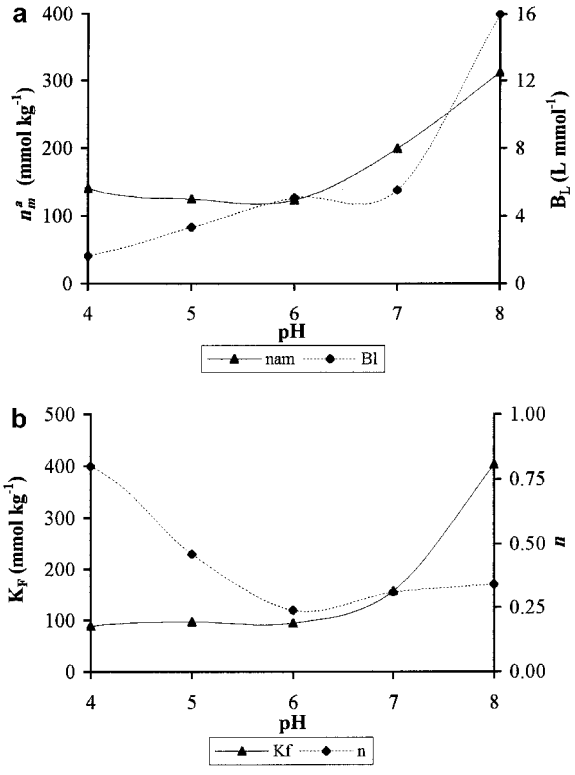


Figure 2. Langmuir (a) and Freundlich (b) parameters deduced from the constant-pH adsorption isotherms of Cd on illite at 25°C and 0.01 M $NaNO_3$.

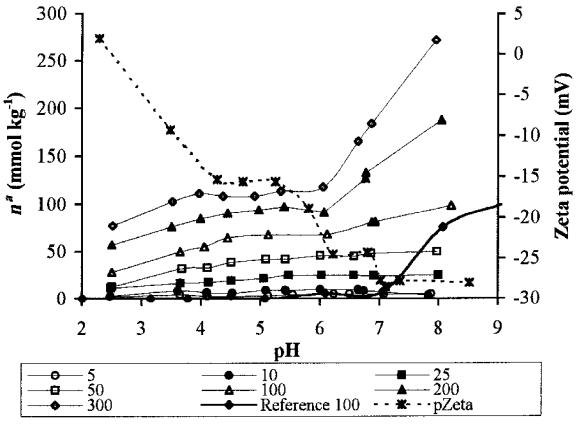


Figure 3. Effect of equilibrium solution pH on Cd sorption on illite at 25°C and 0.01 M $NaNO_3$ for different initial concentrations of Cd (mmol kg^{-1}).

slopes of the plots increased with pH. For the isotherm without illite, the adsorption edge started at pH 7, and represents the precipitation front (Basta and Tabatabai, 1992).

Information on the relationship between the adsorption of metals and the release of protons can be obtained by linearization of a general overall mass action equation for adsorption, including hydrolysis, adsorption and exchange reactions (Spark *et al.*, 1995)

$$\log\frac{[SM]}{[S][M]} \supset \chi\text{pH} \quad \log k \qquad (2)$$

where $[SM]$ is the concentration of adsorbed species, $[S]$ is the concentration of vacant sites, $[M]$ is the total concentration of metal species in solution that in the range studied is approximately equal to $[M^{2+}]$ (Naidu *et al.*, 1994), χ is the proton coefficient, and k is an overall equilibrium constant. If k is independent of pH, then the value of χ obtained from a graph of $\log([SM]/[M])$ against pH indicates the overall proton stoichiometry of the adsorption equilibrium. The release of protons may be associated with reactions at the surface, metal hydrolysis in solution or at the surface, hydrolysis of the adsorbent surface, or a combination of these (McKenzie, 1980).

Table 4 presents the proton stoichiometries obtained by applying the Kurbatov plot for Cd initial concentrations equivalent to 50, 100, 200 and 300 mmol kg^{-1}. It does not include initial concentrations <50 mmol kg^{-1} because the experimental data did not fit this model. In no case was χ a whole number, so it is not possible to conclude that only one metallic species participated in the retention. The proton stoichiometry was higher in the pH range 6–8, lower at more acidic pH, and close to zero at intermediate pH. As the initial amount of Cd increased, χ decreased. The fact that the proton stoichiometry decreased in the more acidic pHs when increasing the initial amount of Cd, and that it was close to zero at intermediate pH indicates that it is not likely that the released protons, in the pH range 2.5–4, came from the formation of hydroxylated species of Cd. The results are consistent with ionic exchange of Cd for the

Table 4. Proton stoichiometry for adsorption of Cd by illite.

Initial concentration (mmol kg^{-1})	Section 1 pH	χ	r^2	Section 2 pH	χ	r^2	Section 3 pH	χ	r^2
50	2.5–3.5	0.60	1	4.5–7.8	0.33	0.91	*	*	*
100	2.5–4.5	0.34	0.99	4.4–6	0.04	0.82	6–8	0.74	0.95
200	2.5–4	0.14	0.95	4–6	0.03	0.28	6–8	0.65	0.98
300	#	#	#	#	#	#	6–8	0.63	0.98

* Has only two sections
\# Has only one section

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H_3O^+ and Na^+ which saturate illite active sites. In the third section ($6 < pH < 8$), proton stoichiometry varied between 0.63 and 0.74, indicating that in addition to ionic exchange Cd^{2+}/Na^+, other hydroxylated species participated.

Figure 3 also shows the variation of zeta potential with pH. The zeta potential was positive for pH values <2.5 (isoelectric point), and negative for pH values >2.5. It decreased in the pH range 2.3–4.3, did not change in the pH range 4.3–5.3, and decreased sharply between pH 5.3 and 7.0. The variation of the amount retained with pH approximately mirrors the variation of amount retained with pH. The decrease in zeta potential in the pH range 2.5–4.3 can be associated with the dissociation of H_3O^+ that neutralize the structural negative charge of illite. On the other hand, the decrease in zeta potential between pH 5.3 and 7 should arise from dissociation of silanol and aluminol groups, in which the specific adsorption of Cd can take place.

Simultaneous effect of pH, initial concentration, ionic strength and temperature on the retention of Cd on illite

For the two experiments, which varied only in the pH range, regression techniques were used to fit the coded parameters (Tables 2 and 3) to a response surface. The equation that describes the amount of Cd adsorbed on illite (mmol kg^{-1}) from pH 3 to 8 in terms of the significant variables, expressed as coded values, is as follows:

$$n^a = 61.4 - 24.5\log[NaNO_3] + 20.5c_0 + 16.4pH - 3.77\log^2[NaNO_3] + 3.04pH^2 - 2.65c_0^2 + 6.14pHc_0 \quad (3)$$

The standard error based on total error with 22 degrees of freedom was ±1.921. A variable was significant if its effect was greater than twice the standard error of that variable. According to the coefficients of the terms of equation 3, between pH 3 and 8, the amount of Cd retained depended mainly on the ionic strength (log [$NaNO_3$]), initial concentration of Cd, and pH. The fact that temperature did not significantly affect the amount of Cd adsorbed, and that concentration of the inert electrolyte was the largest factor suggest that the retention of Cd on illite is basically an electrostatic process, and therefore of low specificity.

Because adsorption edges showed that the amount retained increased sharply for pH >6, a new experiment was performed in the pH range 6–8 keeping the other variables constant. The response surface of the amount of Cd adsorbed (mmol kg^{-1}) in the pH range 6–8 can be expressed by the following equation, in which the variable values are codified (Table 3)

$$n^a = 95.5 + 43.8c_0 - 26.1\log[NaNO_3] + 16.4pH + 4.46T - 3.18\log^2[NaNO_3] + 3.11pH^2 - 2.36c_0^2 + 9.51pHc_0 - 8.27c_0\log[NaNO_3] \quad (4)$$

The standard error based on total error with 21 degrees of freedom was ±1.771. The independent term was larger in the pH range 6–8, reflecting the increase of the retention of Cd as pH increase. The linear effects that were significant in this pH range were the initial amount of Cd, ionic strength (log [$NaNO_3$]), pH, and temperature. The quadratic terms of ionic strength and pH, together with the interaction terms pH-initial concentration of Cd, and initial concentration of Cd-log [$NaNO_3$] were also significant. The interaction pH-initial concentration of Cd was close to the significance limit.

Because it was not possible to plot simultaneously the experimental response as a function of the significant variables that control the adsorption process, we will consider separately the effects of two variables on the response following the order of magnitude observed in the pH range 3–8, and studying at the same time the same effects in the more restricted pH range. Finally, we will deal with the effect of temperature on the amount of Cd adsorbed between pH 6 and 8, the pH range where it significantly affected the response.

Figure 4 shows the simultaneous effect of ionic strength and initial concentration on the amount of Cd adsorbed, at 25°C, and pH values of 5.3 (Figure 4a) and 7.0 (Figure 4b), respectively. Increasing the initial amount of added metal increased the amount of Cd adsorbed on illite; whereas increasing the ionic strength (log [$NaNO_3$]) of the equilibrium solution decreased the amount retained. For a pH value of 7, the retention

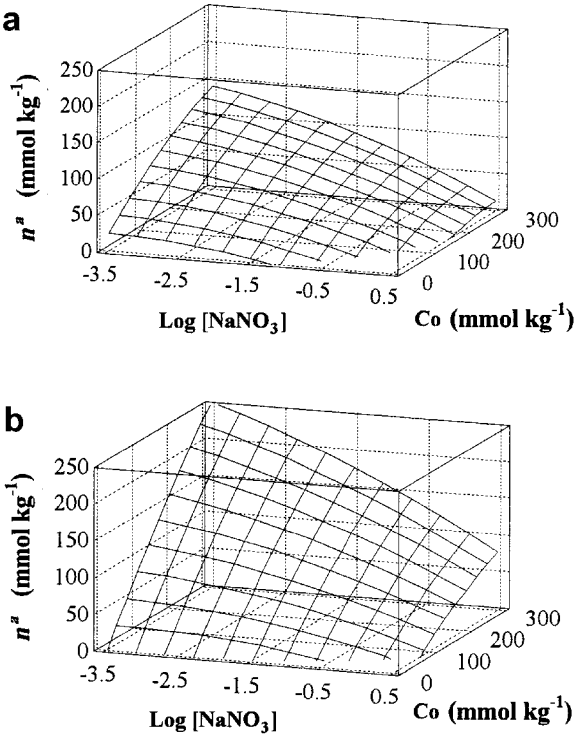


Figure 4. Cd adsorbed on illite (n^a) at 25°C as a function of ionic strength and initial concentration of Cd: (a) pH 5.3, (b) pH 7.0.

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maximum was 250 mmol kg^{-1}, whereas at pH 5.3 the maximum was 145 mmol kg^{-1}.

Figure 5 shows the effect of pH and the concentration of $NaNO_3$ on the concentration of Cd adsorbed on illite for an initial concentration of Cd equivalent to 150 mmol kg^{-1}, and a temperature of 25°C. Independently of pH, and in both pH ranges, the amount adsorbed was largest for the lowest concentrations of $NaNO_3$. The amount of Cd retained decreased markedly for $NaNO_3$ concentrations >0.01 M. For pH <5.5, an initial concentration of Cd equivalent to 150 mmol kg^{-1}, and high concentrations of $NaNO_3$ retention of Cd was practically zero (Figure 5a). The increase in pH favored the adsorption of Cd on illite, but the effect of the ionic strength on the retention decreased with pH. At pH 8 and $NaNO_3$ concentrations <0.1 M, all the Cd initially added (150 mmol kg^{-1}) was retained on illite; for electrolyte concentrations >0.1 M, the amount retained decreased slightly with increasing ionic strength. These results show that the retention mechanisms changed with pH. At acidic pH, Cd was mainly retained by ionic exchange as it was displaced from illite by an inert electrolyte. According to Lützenkirchen (1997), if an increase in ionic strength results in a decrease of ion uptake, the mechanism is believed to be of the outer sphere type, and it is explained by competition of an ion from the supporting electrolyte for the surface functional groups. Insensitivity to ionic strength has been taken as an indication for inner-sphere surface complexation.

Figure 6 illustrates the effect of pH and initial concentration on the retention of Cd on illite at 25°C. The 3-dimensional plot can be compared with the adsorption edges included in Figure 3, with the difference that adsorption edges were obtained at 0.01 M $NaNO_3$ concentration and the response surface was determined at 3.2×10^{-2} M ($\log[NaNO_3] = -1.5$). The amount of Cd adsorbed increased with the initial amount of Cd and the pH. For pH values <4, the amount of Cd adsorbed tended towards a plateau, whereas for pH values >4, the amount adsorbed increased linearly after the inflexion of the adsorption curves. Similar to adsorption edges, for initial concentrations of Cd $\leqslant 10$ mmol kg^{-1}, the amount adsorbed was close to the initial amount; therefore the pH had little effect on the amount retained. For initial concentrations >10 mmol kg^{-1}, retention of Cd was favored by increasing pH. The main difference between the two pH ranges studied was in the magnitude of the amount adsorbed (Figure 6a,b). At pH 8, the amount of Cd retained was proportional to the initial concentration, and its magnitude was practically 100%.

In the pH range 6–8, increasing the temperature slightly favored the retention of Cd on illite. Therefore, the process must be endothermic. The effect increased

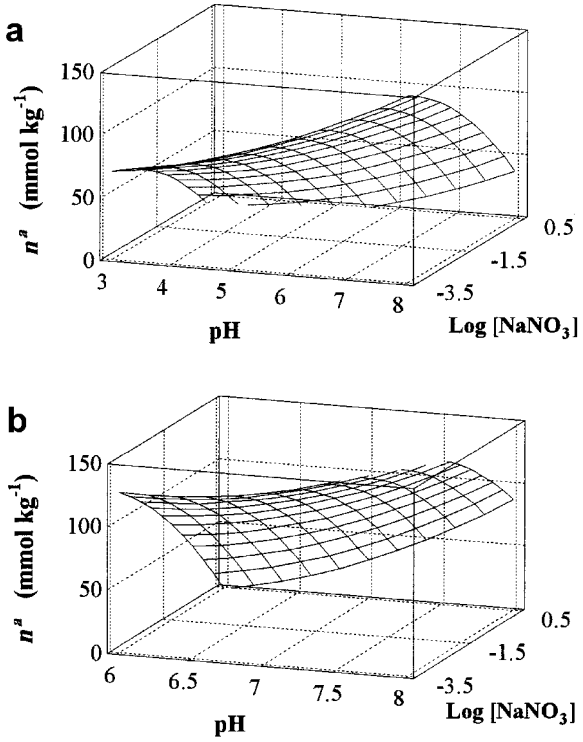


Figure 5. Effect of pH and $NaNO_3$ concentration on the amount of Cd adsorbed on illite for an initial concentration of Cd equivalent to 150 mmol kg^{-1}, and a temperature of 25°C.

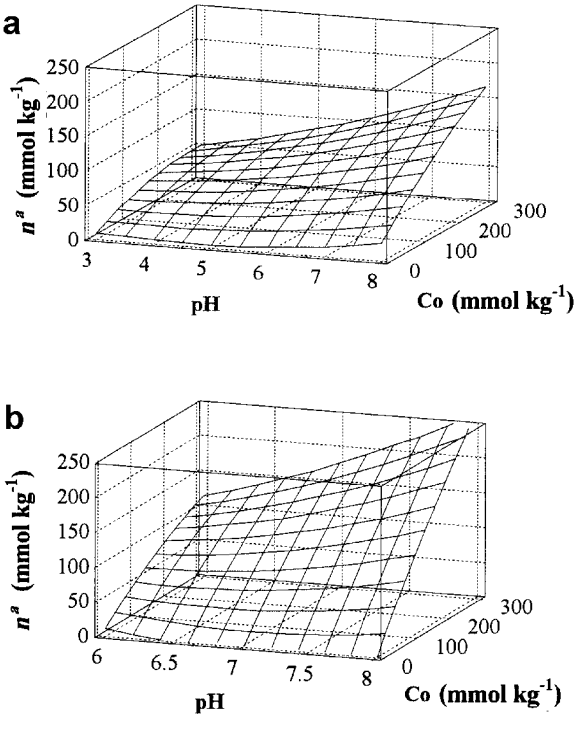


Figure 6. Cd adsorbed on illite (n^a) *vs.* pH and Cd initial concentration at 25°C and 0.032 M $NaNO_3$: (a) pH range 3–8, (b) pH range 6–8.

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with the initial amount of Cd, ionic strength and pH (Figure 7). For an initial concentration equivalent to 300 mmol kg^{-1}, pH 7 and 3.2×10^{-2} M concentration of $NaNO_3$, increasing the temperature from 5 to 45°C led to an increase in the amount of Cd retained from ~170 mmol kg^{-1} to 200 mmol kg^{-1} (Figure 7a). The effect of temperature increased as pH increased. For instance, at pH 6 the amount of Cd retained was independent of temperature; but, at pH 8 (initial concentration of Cd equivalent to 150 mmol kg^{-1}, 3.2×10^{-2} M $NaNO_3$), the amount retained increased from 135 mmol kg^{-1} at 5°C to 150 mmol kg^{-1} (100%) at 35°C (Figure 7b). At pH 6 or lower, ionic exchange prevails, the forces that take part

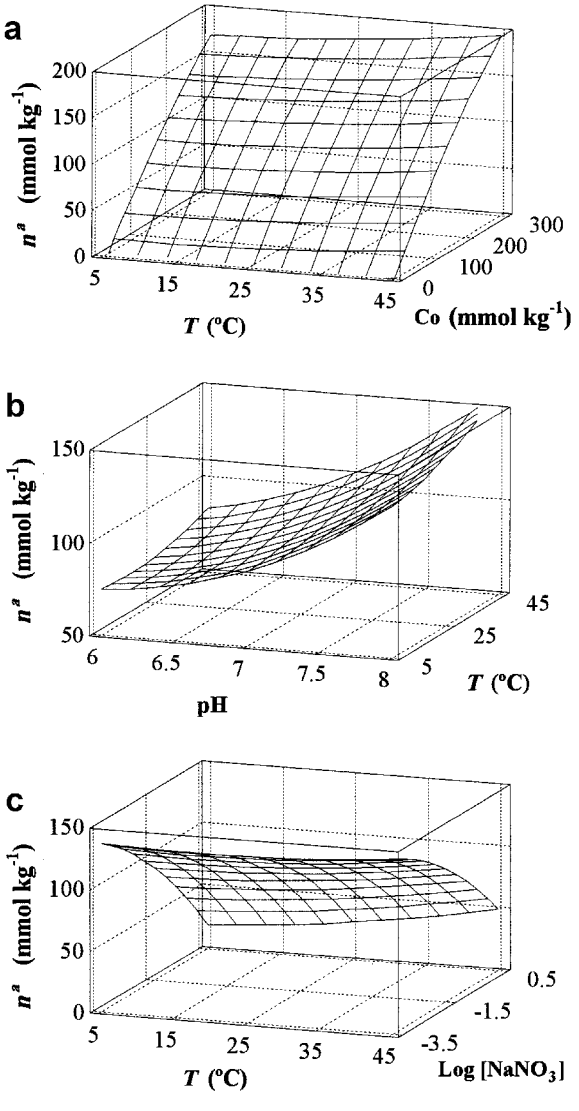


Figure 7. Effect of temperature on the retention of Cd on illite: (a) temperature-initial concentration at pH 7 and 0.032 M $NaNO_3$; (b) temperature-ionic strength at pH 7, and an initial concentration equivalent to 150 mmol kg^{-1}; and (c) temperature-pH at 0.032 M $NaNO_3$ and an initial concentration equivalent to 150 mmol kg^{-1}.

are electrostatic in nature, and the effect of the temperature on retention is less than at higher pH, where other more specific retention mechanisms, including metal-oxygen bonds and the formation of hydroxylated species, occur. It is in the more specific retention mechanisms where the effect of the temperature on the retention is greater. The effect of the temperature was also enhanced for concentrated $NaNO_3$ solutions, where the amount of Cd adsorbed varied from, ~15 mmol kg^{-1} at 5°C to 50 mmol kg^{-1} at 45°C (Figure 7c). The effect decreased with ionic strength, being almost zero at 0.001 M $NaNO_3$ concentration.

The thermodynamic parameters ΔG, ΔH and ΔS of ion adsorption were obtained from the Langmuir apparent equilibrium constant and the van't Hoff equation (Angove *et al.*, 1998). The enthalpy of the reaction was 1.09 kJ mol^{-1}, the entropy variation was 12.9 J mol^{-1} K^{-1}, and the Gibbs free energy was −2.76 kJ mol^{-1}. These values are smaller than those gathered by McBride (1994) for the retention of alkaline earth metals and divalent cations on smectite. Enthalpy variation ranged from 8.03 to 16.2 kJ mol^{-1}; however, those results corresponded to the Cd^{2+}/NH_4^+ or Cd^{2+}/K^+ exchange systems, not to Cd^{2+}/Na^+ system.

Retention mechanisms

The retention of Cd on illite could be described by a model that assumes different binding mechanisms. Below pH 6, adsorption is via ion exchange with H^+ and Na^+ ions that saturate the exchange sites (Pinskii, 1998). The fact that the amount of Cd^{2+} retained on illite decreased as the concentration of $NaNO_3$ increased, to as low as zero for 1 M $NaNO_3$ (Figure 5a), supports this hypothesis. The proton stoichiometry of the exchange process increased with decreasing pH and the initial concentration of Cd^{2+}. Between pH 4.5 and 6, proton stoichiometry was ~0.04, indicating that retention was mainly by ionic exchange with Na^+; below pH 4.5, proton stoichiometry varied from 0.14 for an initial concentration of Cd^{2+} of 200 mmol kg^{-1} to 0.60 for an initial concentration of 50 mmol kg^{-1}. The decrease of proton stoichiometry with the increase of the initial amount of Cd suggests that the exchange H^+/Cd^{2+} is favored over the Na^+/Cd^{2+} exchange. The exchange involving hydrated Cd^{2+} can be depicted by two elementary reactions:

(a) exchange with hydronium ions,

$$2 \equiv S\text{–H} + Cd^{2+}_{(aq)} \rightleftharpoons \equiv S_2\text{–Cd} + 2H^+_{(aq)} \qquad (5)$$

where $\equiv S$ is the active site;

(b) exchange with Na^+ ions,

$$2 \equiv S\text{–Na} + Cd^{2+}_{(aq)} \rightleftharpoons \equiv S_2\text{–Cd} + 2Na^+_{(aq)} \qquad (6)$$

in this case, without involving hydronium ions; consequently, retention of Cd^{2+} should be independent of pH.

For pH values >6, the effect of $NaNO_3$ concentration on the amount of Cd^{2+} retained decreased with pH, being negligible at pH 8; the proton stoichiometry was greater

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than for pH values <6; and the temperature affected the process. These facts are compatible with a more specific process involving hydrolyzed species, in which Cd can associate with illite as an inner sphere complex via covalent bonds between the metal and the electron donating oxygen ions of the surface. It may include several elementary reactions (Pinskii, 1998):
(a) the hydrolysis of Cd^{2+} in solution

$$Cd^{2+} + nH_2O \rightleftharpoons Cd(OH)_m(H_2O)_{n-m}^{2-m} + mH_{(aq)}^{+} \quad (7)$$

with $m < n$, and exchange with hydrolysed species

$$\equiv S\text{–Na} + Cd(OH)_m(H_2O)_{n-m}^{2-m} \rightleftharpoons \equiv S\text{–CdOH} + Na_{(aq)}^{+} \quad (8)$$

(b) another variant is simultaneous hydrolysis and exchange of hydrated ions

$$\equiv S\text{–Na} + H_2O + Cd_{(aq)}^{2+} \rightleftharpoons \equiv S\text{–CdOH} + Na_{(aq)}^{+} + H_{(aq)}^{+} \quad (9)$$

In both cases, the equilibrium solution is acidified, with the extent of acidification depending on the affinity of active surface sites with Cd^{2+}, $CdOH^{+}$ cations, and the hydronium ions released during the hydrolysis.

Another retention mechanism compatible with the release of hydronium ions would be the precipitation of $Cd(OH)_2$

$$Cd_{(aq)}^{2+} + 2H_2O \rightleftharpoons Cd(OH)_{2(s)} + 2H_{(aq)}^{+} \quad (10)$$

Two limiting cases for the initiation of precipitation are the heterogenous model and the surface precipitation. In the heterogenous nucleation model, the interface is fixed and no mixing of ions occurs across the interface. As a consequence, precipitation of the new solid phase does not occur until the solution becomes supersaturated. In the surface precipitation model, the interface is a mixing zone for the ions of the new solid phase and those of the substrate. The surface phase is treated as an ideal solid-solution. This allows precipitation to start from solutions undersaturated with the pure phase (Stumm, 1992). The adsorption edge for a solution of Cd^{2+} equivalent to 100 mmol kg^{-1} in 0.01 M $NaNO_3$ and 25°C, shows that heterogenous precipitation started at ~pH 7; in the presence of illite, the adsorption edges started at pH 6. At low concentrations, adsorption processes are able to maintain solubility at a level too low for precipitation to occur. Nevertheless, in situations with high metal loadings and high pH, heterogenous precipitation will predominate (McBride, 1989).

The hydrolytic and precipitation processes can occur simultaneously. With the experimental techniques used we do not have direct evidence as to which of them is taking place and in what proportion. In any case, this is an open field for future research.

CONCLUSIONS

The initial slope of the adsorption isotherms and the amount of Cd adsorbed by illite increased with pH. Proton stoichiometry deduced from adsorption edges was higher in the pH range 6–8, lower at more acidic pH, and close to zero at intermediate pH. Response surface methodology showed that the amount of Cd retained depended mainly on the ionic strength, initial concentration of Cd, and pH. The temperature had a significant effect only in the pH range 6–8. The thermodynamic parameters deduced from the Langmuir apparent equilibrium constant at pH 7 and the van't Hoff equation were ΔH = 1.09 kJ mol^{-1}, ΔS + 12.9 J mol^{-1} K^{-1} and ΔG = −2.76 kJ mol^{-1}. The retention of Cd on illite could be described by a model that assumes different binding mechanisms. Below pH 4.5, adsorption was via ion exchange with H^{+} and Na^{+} ions that saturate exchange sites. The exchange H^{+}/Cd^{2+} was favored over the Na^{+}/Cd^{2+} exchange. For pH values >6, more specific processes involving hydrolyzed species took place.

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