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Adsorption of copper, cadmium and lead from aqueous solution to the kaolinite/water interface

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Abstract

The adsorption of Cu(II), Cd(II) and Pb(II) from aqueous solution to the kaolinite/water interface has been studied at 298.2 K as a function of both pH and ionic strength of the aqueous phase. The extent of adsorption increases with increasing pH and with decreasing ionic strength. Both effects can be explained by a model that assumes two kinds of binding sites: a) weakly acidic groups XH that account for ion exchange, and b) ampholytic surface hydroxyls SOH which form inner sphere complexes with the divalent metal ions.

Introduction

The mobility of metal ions in the soil column and their availability to plants is largely governed by processes of the general scheme (Schindler, 1984; Tiller, 1986)

$$\text{dissolved metal} = \text{particulate metal} \qquad (1)$$

Typical examples are:

$$Ca^{2+} + 2\,HCO_3^- = CaCO_{3(s)} + CO_{2(g)} + H_2O$$

$$Al^{3+} + 3\,H_2O = Al(OH)_{3(s)} + 3\,H^+$$

$$M^{z+}, \text{oxide/clay particles} = M^{z+} \text{ adsorbed at oxide/clay particles}, H^+$$

In many cases the reactions comprised by Equation 1 tend to approach the thermodynamic equilibrium. The partition of a given component between soil solution and soil minerals is then at least approximately described by the pertinent equilibrium constants. The classical approach (Lindsay, 1979) assumes pure solids as the controlling phases: the soil solution is understood as a saturated solution of the soil minerals present. Whereas this concept applies to components such as Fe(III) and Mn(IV), it was noted that observed concentrations of both Cu(II) and Zn(II) are much lower than those calculated on the basis of the solubilities of the corresponding oxides, hydroxides and carbonates (Lindsay, 1972). This suggests that the concentrations of some trace metals are controlled by adsorption/desorption reactions rather than by solubility equilibria (Ellis & Knezek, 1972 and older literature quoted therein; Sposito, 1984a).

Adsorption of heavy metals at oxide/water interfaces can conveniently be described as surface complexation (Schindler, 1981; Sposito, 1984b; Westall, 1986; Schindler & Stumm, 1987):

$$n\,\mathrm{SOH} + \mathrm{M}^{z+} = (\mathrm{SO})_n\mathrm{M}^{(z-n)+} + n\,\mathrm{H}^+$$

The uptake of heavy metals by clay minerals is obviously more complicated. At low pH values unspecific bonding based on electrostatic interaction of the hydrated metal ions with the negatively charged aluminosilicate matrix is the dominating process (McBride, 1976). X-ray photoelectron spectroscopy reveals that (for Co(II)-kaolinite) the chemical nature of the metal-clay interaction changes with increasing pH (Dillard & Koppelman, 1982). This pH dependence of both the extent of heavy metal uptake and the nature of the metal-clay bond is in turn reflected by the fact (Menzel & Jackson, 1951) that at elevated pH values the uptake of heavy metal ions is accompanied by a release of hydrogen ions. Moreover, uptake of heavy metals at elevated pH values seems to be much more specific than uptake at low pH. Farrah et al. (1980) thus concluded that the classical ion exchange model does not cover the whole range of adsorption phenomena and that part of the heavy metal adsorption occurs at sites created by displacement of protons from surface hydroxyls. This latter mode is indeed identical with the above mentioned surface complexation.

This paper reports on the uptake of Cu(II), Cd(II) and Pb(II) by kaolinite as a function of both pH and ionic strength. An attempt is made to explain the obtained data with a combined ion exchange-surface complexation model.

Experimental part

Survey

Portions of A kg of kaolinite were suspended in Vo dm^3 of solutions S1 of the general composition

S1: $[\mathrm{M}^{2+}] = \mathrm{Bo}$ M
$[\mathrm{H}^+] = \mathrm{Ho}$ M
$[\mathrm{Na}^+] = (\mathrm{I} - 2\mathrm{Bo} - \mathrm{Ho})$ M
$[\mathrm{ClO}_4^-] = \mathrm{I}$ M

and potentiometrically titrated at 298.2 K with V dm^3 of solutions S2 of the general composition

S2: $[OH^-] = Co$ M
$[Na^+] = (Co + I)$ M
$[ClO_4^-] = I$ M

After each addition of base and a subsequent equilibration time of 10 minutes, both $[H^+]$ and $[M^{2+}]$ were obtained from electromotive force (emf) measurements with glass electrodes and M^{2+}-specific electrodes. Some titrations were carried out in the absence of M^{2+}. The parameters Bo and I were varied as follows:

$Bo \approx 1.E\text{-}4\,M\ (9.1\,E\text{-}5\,M - 9.9\,E\text{-}5M)$ I: 0.01, 0.1, 1.0 M

The ratio A/Vo was kept close to 0.02 kg/dm^3. The so obtained titration curves were reproducible but only partially reversible. This means that the subsequent application of equilibrium thermodynamics is only a first approximation.

The percentage of adsorbed divalent metal was obtained from

$$\%\,M(II)_{ads} = 100([M(II)]_t - [M(II)]_d)/[M(II)]_t \qquad (2)$$

The total concentration $[M(II)]_t$ of divalent metal in the suspension is given by

$$[M(II)]_t = VoBo/(Vo + V)$$

and the total concentration $[M(II)]_d$ of dissolved divalent metal is related to $[M^{2+}]$ by

$$[M(II)]_d = [M^{2+}](1 + \Sigma{*}\beta_n[H^+]^{-n})$$

where ${*}\beta_n$ is the stability constant of the hydroxo complex $M(OH)_n^{(2-n)+}$.

The experimental data were further combined to obtain H*, the number of moles of hydrogen ions per dm^3 of solution that originates from the kaolinite-water interface:

$$H{*} = [H^+] - H_a$$

H_a, the analytical hydrogen ion concentration (i.e. the hydrogen ion concentration that one would observe in the absence of clay) is accessible from

$$H_a = (VoHo - VCo)/(Vo + V) + [OH^-] + \Sigma n{*}\beta_n[M^{2+}][H^+]^{-n} \qquad (3)$$

The last term on the right hand side of Eq. 3 accounts for hydrogen ions formed in the course of the hydrolysis of M^{2+}.

Materials

Georgia kaolinite (KGa-1) was obtained from The Clay Minerals Society. The heteroionic material was repeatedly treated with $HClO_4$, H_2O_2 and NaOH. Details are given elsewhere (Liechti, 1982). The final treatment consisted of reacting with 0.001 M $HClO_4$ followed by repeated washing with bidistilled water (until constant conductivity was observed) and lyophilization. The whole procedure took usually several days. Hence the term 'freshly prepared' as used below refers to a moderately aged (2-5 days old) sample. The so obtained H-clay is not stable (Ferris & Jepson, 1975). Titration curves of samples that had been stored for 4 months differed significantly from curves obtained with freshly prepared samples. The curves discussed in this report reflect the properties of freshly prepared H-kaolinite. BET surface area $S = 10200\ m^2/kg$. Total amount of ionizable groups (estimated according to Schindler & Kamber, 1968): $S^o = 5.55$ E-2 mol/kg.

$NaClO_4$ was prepared from $HClO_4$ and Na_2CO_3 (analytical grade, Merck) as described earlier (Santschi & Schindler, 1974). Stock solutions of $Cu(ClO_4)_2$, $Cd(ClO_4)_2$ and $Pb(ClO_4)_2$ were obtained from analytical grade CuO, $CdCO_3$, PbO and $HClO_4$ and standardized against EDTA. Solutions of NaOH were prepared from Titrisol (Merck) and standardized coulometrically.

Electromotive force measurements

The concentrations of hydrogen ions and metal ions were obtained with the aid of the cells

RE / I M $NaClO_4$ / glass electrode (a)
RE / I M $NaClO_4$ / M^{2+}-sensitive electrode (b)
where RE is the reference electrode
Ag, AgCl / 0.01 I M NaCl, 0.99 I M $NaClO_4$.

Metrohm (EA 109) glass electrodes and Orion ion-sensitive electrodes were used. A Wilhelm-type salt bridge (Forsling et al., 1952) was used to connect test solution and reference electrode. Under the prevailing experimental conditions, variations in the liquid junction potential between the salt bridge and the test solutions could be neglected. The emf of the cells are thus given by

$$E_a = E_a^o + k_a \log [H^+]$$
$$E_b = E_b^o + k_b \log [M^{2+}]$$

E_a^o, k_a, E_b^o and k_b were obtained from separate calibrations. It should be emphasized that the quantity obtained from emf measurements with cell a is the hydrogen ion concentration. The pH values as used in this report are defined by

$$pH = -\log [H^+] y_H$$

where y_H is the activity coefficient of the hydrogen ions obtained from the Davies equation (see below).

Auxiliary contants

Stability constants of the hydroxo complexes of Cu^{2+}, Cd^{2+} and Pb^{2+} were taken from Baes & Mesmer (1976).

Results and discussion

The titration curves of H-kaolinite (Fig. 1) display two buffer regions separated by approximately 1.5 pH units. This indicates the presence of two kinds of acidic groups. The adsorption data (Figs. 2-4) show a striking effect of the ionic strength, i.e. of the prevailing sodium concentration. At low pH values the sodium ions can successfully compete with the divalent metal ions and $NaClO_4$ suppresses adsorption up to pH 4.5 (Cu(II), Pb(II)) and pH 6 (Cd(II)) respectively. At higher pH values, however, even high concentrations of background electrolyte cannot prevent the divalent metal ions from being adsorbed. These observations suggest two different sites for M(II) binding. We thus postulate that the kaolinite sample contains

- weakly acidic groups XH which are able to undergo ion exchange with both Na^+ and M^{2+} ions. The total concentration of these groups is obtained from Fig. 1: $\{XH\}_t = 1.56$ E-2 moles/kg.
- ampholytic surface hydroxyls SOH which can bind and release protons (to give SO^- and SOH_2^+) and to form inner sphere complexes SOM^+ and $(SO)_2M$. In addition, they are assumed to bind Na^+ by forming a weak outer sphere complex SO^-Na^+. The total concentration of SOH groups is

$$\{SOH\}_t = S^0 - \{XH\}_t = 3.99 \text{ E-2 moles/kg}$$

Specifically we postulate the following equilibria:

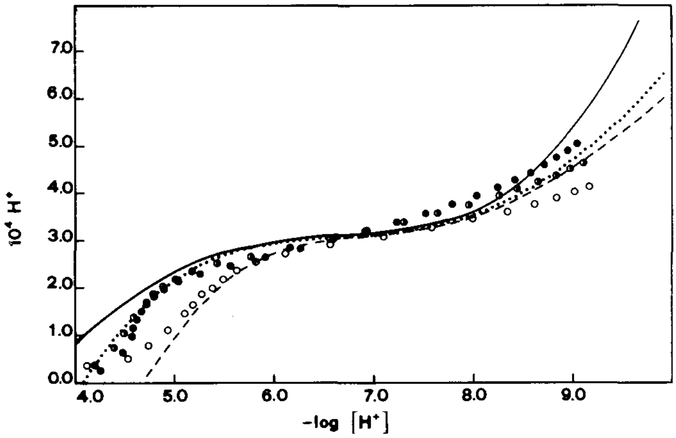

Fig. 1. Titration of H-kaolinite with NaOH; H* as a function of log [H⁺]. The drawn lines are calculated with the constants given in Table 1. I = 0.01: – – – and open circles; I = 0.1: . . . . and half-filled circles; I = 1.0: —— and filled circles.

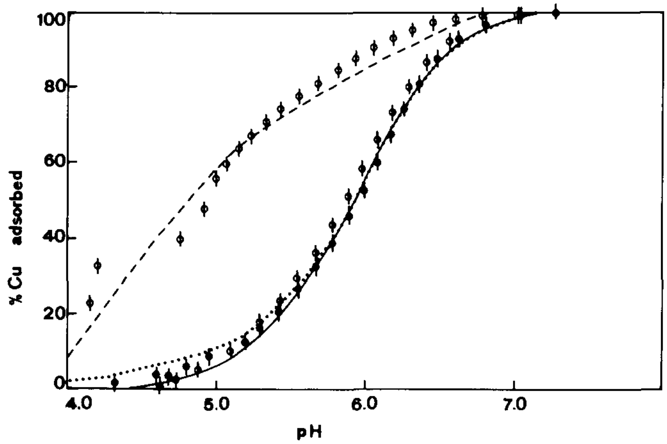

Fig. 2. Adsorption of Cu(II) by kaolinite as a function of log $[H^+]$. The drawn lines are calculated with the constants given in Table 1. For explanation of symbols, see Fig. 1.

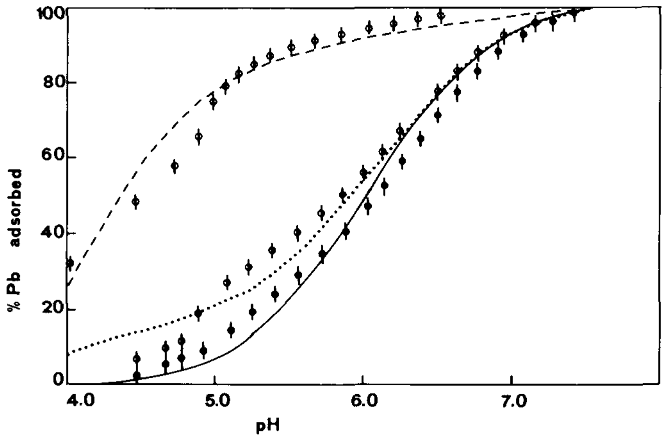

Fig. 3. Adsorption of Pb(II) by kaolinite as a function of log $[H^+]$. The drawn lines are calculated with the constants given in Table 1. For explanation of symbols, see Fig. 1.

$$XNa + H^+ = XH + Na^+$$

$$K_1 = \{XH\}[Na^+]y_{Na}/\{XNa\}[H^+]y_H$$

$$2\,XNa + M^{2+} = X_2M + 2\,Na^+$$

$$K_2 = \{X_2M\}[Na]^2y^2_{Na}/\{XNa\}^2[M^{2+}]y_M$$

$$SOH + Na^+ = SONa + H^+$$

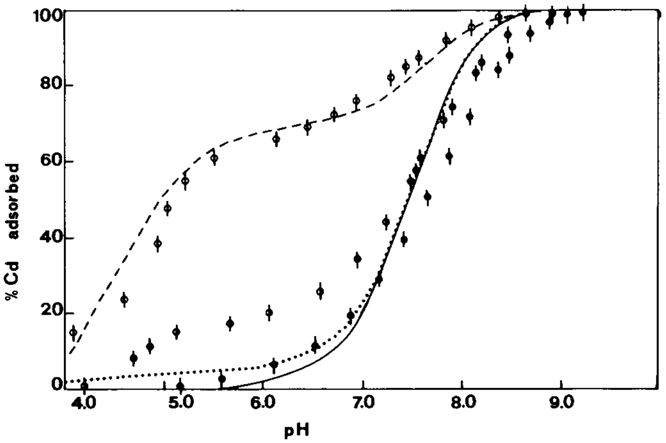

Fig. 4. Adsorption of Cd(II) by kaolinite as a function of log $[H^+]$. The drawn lines are calculated with the constants given in Table 1. For explanation of symbols, see Fig. 1.

$$K_3 = \{SONa\}[H^+]y_H/\{SOH\}[Na^+]y_{Na}$$

$$SOH_2^+ = SOH + H^+$$

$$*K_{a1}^s = \{SOH\}[H^+]y_H \exp(-F\psi/RT)/\{SOH_2^+\}$$

$$SOH = SO^- + H^+$$

$$*K_{a2}^s = \{SO^-\}[H^+]y_H \exp(-F\psi/RT)\{SOH\}$$

$$SOH + M^{2+} = SOM^+ + H^+$$

$$*K_1^s = \{SOM^+\}[H^+]y_H \exp(F\psi/RT)/\{SOH\}[M^{2+}]y_M$$

$$2\,SOH + M^{2+} = (SO)_2M + 2H^+$$

$$*\beta_2^s = \{(SO)_2M\}[H^+]^2y^2_H/\{SOH\}^2[M^{2+}]y_M$$

where ψ stands for the acting surface potential. ψ was calculated on the basis of the constant capacitance model (Schindler & Gamsjäger, 1972):

$$\psi = (\{SOH_2^+\} + \{SOM^+\} - \{SO^-\})*F/S*\kappa,$$

where F is the Faraday constant and κ is the specific capacitance. The activity coefficients of the dissolved species were obtained from the Davies equation (Davies, 1962, p. 41)

Table 1. Equilibrium constants 298.2 K, I = 0.

$\log K_1 = 2.9$ $\qquad$ $\log K_3 = -9.84$
$\log K^s_{a1} = -4.37$ $\qquad$ $\log K^s_{a2} = -9.18$

	Cu(II)	Cd(II)	Pb(II)
$\log K_2$	2.39	2.27	2.98
K_v	3.83	2.90	14.9
$\log {*K^s_1}$	-2.50	- 4.29	-2.45
$\log {*\beta^s_2}$	-7.46	-10.4	-8.11

$$\log y_i = -0.5\, z_i^2\, (I^{1/2}/(1 + I^{1/2}) - 0.3I).$$

The activity coefficients of the surface species were assumed to be unity. The equilibrium constants were evaluated with the aid of a HP-85 adapted version of FITEQL (Westall, 1982). In a first step, the constants K_1, K_3, K^s_{a1} and K^s_{a2} were evaluated from the data shown in Fig. 1. The calculations were performed with different values for the specific capacitance κ. The best fit was obtained with $\kappa = 2.2$ farad/m^2. In the subsequent steps, the equilibrium constants related to M(II) uptake were evaluated. The obtained values are shown in Table 1. Figures 1-4 indicate that the chosen model gives an acceptable (although not perfect) fit of the experimental data. Systematic errors may originate from

- non-ideal behaviour of the adsorbed species;
- extending the validity range of the Davies equation up to ionic strength 1;
- selecting the same double-layer model and even the same value for the specific capacitance for solutions of very different ionic strength.

Furthermore, the introduction of just two kinds of adsorbing sites is an oversimplification that does not allow for the heterogeneity of the clay. The suitability of a model cannot just be measured by its ability to fit a given set of experimental data. In addition the observed values for the constants of the postulated equilibria must be in accordance with related observations. We therefore compare the properties of the postulated groups XH and SOH (as exhibited by the corresponding equilibria) with properties of ion exchanging groups at clays and with surface hydroxyls at alumina and silica.

The nature of the XH groups

The constants K_2 that describe the ion exchange M^{2+}-Na^+ are related to the more familiar Vanselow coefficients K_v by

$$K_v = K_2\,(\{NaX\} + \{MX_2\}) \approx 1.56\,E-2K_2.$$

The observed values for K_v (Table 1) are somewhat higher than corresponding values reported for montmorillonite (Bruggenwert & Kamphorst, 1982; Sposito et al., 1981). For the exchange

Cd-kaolinite + Pb^{2+} = Pb-kaolinite + Cd^{2+},

however, the reported value of $K_{ex} = 0.31$ (± 0.1) (Bittell & Miller, 1974) is in fair agreement with the present results (Table 1): $K_{ex} = K_v(Cd)/K_v(Pb) = 0.19$. This would indicate that the ion exchange properties of the kaolinite sample are actually represented by the groups XH. On the other hand, K_1 is much larger than reported values for similar systems ($K_1 \approx 1$). This could mean that the assumed H-clay is actually a (H-Al)-clay, a possibility that would be consistent with the actual age of our 'freshly prepared' samples. The left hand side part of the titration curve (Fig. 1) would then describe the Na^+-Al^{3+} exchange and the subsequent hydrolysis of Al^{3+}. The comparatively high value of K_{a1} would then at least partially be related to the first hydrolysis constant of Al^{3+} ($\log *K_1 \approx -5$). Our present data do not permit to unambiguously distinguish between the two possibilities. Further work is planned.

In addition, the question whether the XH or X(H, Al) groups identified in our kaolinite sample are to be ascribed to isomorphous substitution or to contamination with very small amounts of 2:1 phyllosilicates (Talibudeen, 1984) must be left open.

The nature of the SOH groups

The stabilities of the surface complexes of Cu(II) and Pb(II) with deprotonated SiOH and AlOH groups (Table 2, Schindler & Stumm, 1987) are comparatively well known. The comparison with the corresponding values for the kaolinite sample suggests that the postulated SOH groups can be identified as Al-OH groups.

Surface speciation: relative importance of the individual processes

Fig. 5 displays the surface speciation of kaolinite for a system consisting of 1 g of kaolinite suspended in 0.05 dm^3 of 1.E-4 M $Cu(ClO_4)_2$ solutions of different ionic strengths (Systems with Cd(II) and Pb(II) are similar.) First, we note that in the chosen pH range only seven out of the nine postulated surface species are of importance. The concentrations of SO^- and SOH remain marginal. The important feature seen from Fig. 5 is the demonstration of how the relative importance of ion exchange and surface complexation is governed by the prevailing ionic strength, i.e. by the concentration of the sodium ions. At I = 0.01 (what is approximately the ionic strength of soil solutions and fresh waters) and for Cu(II), ion exchange domi-

Table 2. Stability constants of surface complexes with AlOH and SiOH groups (Schindler & Stumm, 1987).

		Cu(II)	Pb(II)
AlOH			
$\log *K_1^s$	(0.1 M $NaClO_4$)	− 2.1	− 2.2
$\log *\beta_2^s$	(0.1 M $NaClO_4$)	− 7.0	− 8.1
SiOH			
$\log *K_1^s$	(1 M $NaClO_4$)	− 5.52	− 5.09
$\log *\beta_2^s$	(1 M $NaClO_4$)	−11.19	−10.68

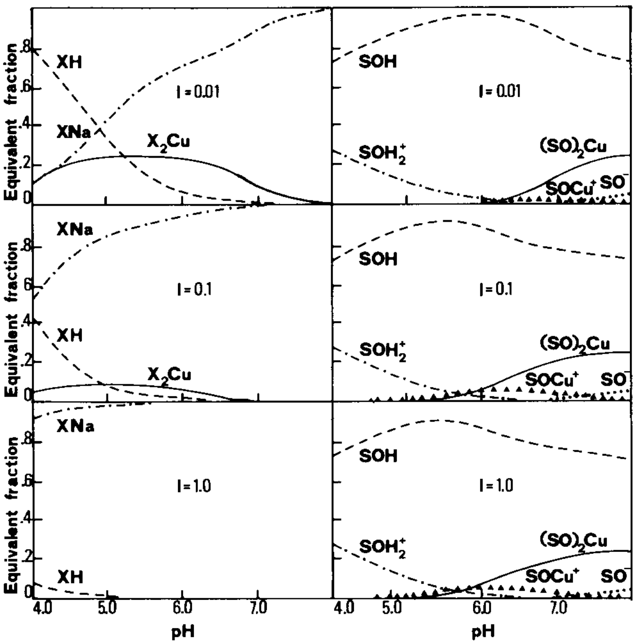

Fig. 5. Surface speciation in the system Cu(II)-NaClO$_4$-kaolinite as a function of pH and I:[Cu(II)]$_t$ = 1.E-4 M, A/Vo = 0.02 kg/dm^3.

nates up to a pH value of 6.5. At I = 1 (and thus, for instance, in sea water) uptake by ion exchange is negligibly small. Finally, it is seen that the relative contributions of the surface complexes $SOCu^+$ and $(SO)_2Cu$ are dependent on I in so far as $SOCu^+$ is unimportant at low ionic strength.

Conclusions

The uptake of heavy metal ions by kaolinite from solutions of various ionic strengths and pH values can approximately be described by a model that assumes two kinds of binding sites:

a) weakly acidic sites XH capable to undergo ion exchange and thus unspecific adsorption;

b) ampholytic surface hydroxyls AlOH responsible for specific adsorption by formation of inner sphere complexes.

The model calculations suggest that ion exchange is important at low pH values and low ionic strength whereas an increase in both ionic strength and pH value favor specific adsorption.

Acknowledgements

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