MODELING ADSORPTION-DESORPTION PROCESSES OF Cu ON EDGE AND PLANAR SITES OF MONTMORILLONITE

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Abstract

The effect of the ionic strength on adsorption of Cu on Ca-montmorillonite (SAz-1) was studied at concentrations ranging from 31 to 516 μM . An adsorption model was employed in the analysis of the data. When the background electrolyte was NaClO_4 the ionic interchange was suppressed at 0.5 M, and Cu adsorption was taking place on edge sites, reaching a plateau at about 24 mmol/kg. A further increase in ionic strength did not make any effect on Cu adsorption, suggesting that the heavy metal was being adsorbed by inner sphere complexes on the edge sites. A binding coefficient for Cu^{2+} on the edge sites $K = 2 \times 10^4 \text{ M}^{-1}$ was determined indicating very high affinity of Cu^{2+} for these sites. When the electrolyte used was NaCl the amounts of Cu adsorbed were reduced. The model predicted well the adsorption data by considering adsorption of CuCl^+ species. Adsorption-desorption processes of Cu on Ca-montmorillonite in media of 0.01 and 0.1 M NaCl showed hysteresis. Model calculations predict the desorbed amounts fairly well. According to the model the hysteresis is mainly attributed to the heterogeneity of sites for the adsorption of Cu. The hysteresis arising from the planar sites is largely due to reduced competition for adsorption and enhancement in the magnitude of the surface potential.

Introduction

Copper content in soils has lately increased as a result of repetitive application of manure, Cu-containing pesticides, sludges, and industrial mine wastes. Vineyard cultivation in soils in Italy where Cu was used for protection against fungal diseases, showed a large copper enrichment in the top soil layer with a decreased concentration gradient along the depth (1). Successive long term applications of municipal sludges on soils have shown to increase the amount of bioavailable Cu and its phytotoxicity (2, 3). The addition of residues such as olive mill wastewater on soils caused a release of the heavy metals previously retained, increasing their leaching, and the hazard of groundwater pollution (4). In this context, adsorption-desorption of copper on laminar silicates is of prime importance since their surfaces show a high affinity for fixation of heavy metals (5, 6).

Studies on the adsorption of the heavy metals on layer silicates have proposed the existence of sites of different affinity, where the higher affinity sites occupy a small fraction of the surface (7-9). The increase in the number of these high affinity sites with increasing pH suggests that they are associated with the edge sites of the silicate layer whereas those of lower affinity are ionic interlayer sites (10, 11). However, the contribution of these sites to copper adsorption-desorption on montmorillonite has not yet been well established. Maqueda et al. (12) suggested that the heterogeneity of adsorption sites affects the adsorption process, and hysteresis is likely to be associated with the different paths of the adsorption and desorption processes.

The adsorption and desorption processes of copper on clay mineral surfaces, and in general, in soils, have mostly been discussed by employing empirical models, such as Freundlich equation, which give a simple description of the experimental data with no particular theoretical basis (13, 14). Mechanistic or surface complexation models,

which are based on thermodynamic concepts, have been applied to copper adsorption on layer silicates (15, 16). No information exists in the literature about their application to desorption processes.

In this article, we try to elucidate the role of the heterogeneity of sites on the adsorption-desorption processes of copper on a layer silicate, such as Ca-montmorillonite, by extending a surface complexation model that was shown to explain consistently the adsorption-desorption processes of cadmium on the same clay mineral (17). In the latter case, the success of the model in predicting experimental results by considering only one type of sites was due to the fact that most of the adsorption was on the planar sites.

In the current work, the model of cation adsorption in closed system (18-20) is further extended to consider adsorption/desorption of Cu (or other cations) on two types of sites of Ca-montmorillonite. The employment of the model and experimental tests permits us to critically evaluate and explain the hysteresis phenomenon.

Experimental Section

Materials

The clay mineral used was a standard montmorillonite from Arizona, designated SAZ-1 (21), supplied by the Clay Mineral Society. Its cation exchange capacity (CEC) is 1.235 mol_c/kg of which 1.0078 mol_c/kg are due to Ca²⁺, 0.1916 mol_c/kg to Mg²⁺, 0.026 mol_c/kg to Na⁺, and 0.0096 mol_c/kg to K⁺ (9).

Standard solutions of copper were supplied by Merck (Darmstadt, Germany). Analytical grade salts NaCl and NaClO₄ were also obtained from Merck; CaCl₂ and MgCl₂ were purchased from Aldrich (Milwaukee, Wisconsin).

Methods

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 Cu concentrations. The range of concentrations used was from 31 to 516 μM . The experiments were carried out in NaClO_4 or NaCl media, the ionic strengths used being 0.01, 0.1, 0.5 and 1.0 M. The samples were shaken for 24 h at 20 ± 1 $^\circ\text{C}$, since preliminary experiments determined that equilibration was reached. Then, the suspensions were centrifuged and the supernatants were analyzed. The concentrations of Cu, Ca and Mg in the supernatants were determined by inductively coupled plasma atomic emission spectrometer, and K was determined by flame photometry. The amounts of Cu adsorbed were determined from the difference between the total concentrations and those in the supernatant.

Adsorption of Cu on SAZ-1 was also determined in solutions containing as a background 0.01 N NaCl and KCl or CsCl at concentrations of 0.5, 5.0 and 10.0 mM. These added results were mainly introduced to test the ability of the model to yield predictions for cases not included in the determination of the parameters.

Desorption experiments were performed after adsorption equilibrium was reached for Cu adsorption in 0.01 and 0.1 M NaCl medium, by removing half of the supernatant after centrifugation, replacing it with 10 ml of 0.01 or 0.1 M, respectively, allowing equilibration for an additional 24 h period, and subsequently continuing as in the adsorption experiment. Preliminary experiments showed that there was no difference in the amount of Cu desorbed in 24 h and two weeks. This process was repeated twice more.

In some desorption points, the removed supernatant was replenished with the solution of the background electrolyte including the amounts of Ca and Mg present in

the volume removed. The desorption experiments proceeded as described before. Ca and Mg were added as $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{ClO}_4)_2$, respectively, in order to keep the equilibrium pH.

Since the clay was not treated previously for the adsorption-desorption experiments, the hypothetical interference of Fe and Al impurities of the clay on Cu adsorption was checked by removing Fe and Al oxides as described in Kunze and Dixon (22), and performing subsequent Cu adsorption at high ionic strengths. The effect of this procedure on the adsorbed amounts of Cu was small (up to 7%).

Model calculations

The cation adsorption model used in this study has been described in Nir (18). The program considers cation binding and the electrostatic Gouy-Chapman equations, and solves iteratively for the solution concentrations of all cations in a closed system. Cation adsorption is obtained by considering specific binding to surface sites and residence in the double layer region. The model was extended to account explicitly for complexation reactions in solution (17). This extension is also essential in studies on the adsorption of copper. In the current study we extended the model to account for cation adsorption on two types of sites, planar (P) and edge (E). The actual extension was introduced into a program which also considers adsorption of organic cations and cations aggregation in solution (19). For brevity we only present a few equations and define the model parameters.

The symbols M_i^+ and M_j^{2+} denote cations that can bind to singly charged negative sites, P^- or E^- , on the planar and edge surfaces of the clay mineral, respectively. The binding reaction for a monovalent cation is :

The respective binding coefficients will be denoted by K_i and K_{iE} , and are given by:

$$K_i = [(PM_i)^0] / ([P^-][M_{i(0)}^+]) \quad (2)$$

in which $[M_{i(0)}^+]$ is the concentration of the cation at the surface. Similarly, K_{iE} is given by an expression which includes $(EM_i)^0$ and E^- .

Divalent cations can react with one surface site yielding a charged complex, or they can associate to form a neutral complex, by binding to a divalent charged site $(P^{2-}) = (P^-)/2$. For neutral complexes:

and similarly,

with K_{2j} and K_{2Ej} defined similarly to K_i and K_{iE} . As was pointed (18), data for adsorption of divalent cations could be fit by considering either charged or neutral complexes. Both modes were considered in a study employing divalent organic cations (23). In the current study with copper we only considered neutral complexes. In equations (1) to (3) the concentrations and binding coefficients are given in units of M and M^{-1} , respectively. The program considers solution complexes, e.g., $(Cu^{2+}Cl^-)^+$ and $(Cu^{2+}Cl_2^-)^0$ and surface complexes, such as $(P^-Cu^{2+}Cl^-)^0$ or $(E^-Cu^{2+}Cl^-)^0$.

The concentration of the cation M_j^{2+} at the surface is:

$$M_j^{2+}(0) = S^{2+}Y_0Z, \quad (4)$$

where $Y_0 = \exp(-e \Psi(0)/kT)$, Z is the valence of the given ion, e is the absolute magnitude of an electronic charge, $\Psi(0)$ is the surface potential, k is Boltzmann's factor, and T is the absolute temperature. $M_j^{2+}(0)$ is the molar concentration of cation j close to the mineral layer, and S^{2+} is the concentration of that cation in the equilibrium solution, far away from the surface.

The excess concentration of mono- and di-valent cations in the double layer region above their bulk concentration (Q_1 and Q_2) can be calculated analytically (18), whereas no limitation on valencies exist in the numerical calculations in the extended program as in Rytwo et al.(19). For a cation of type i and valence z , the excess of its concentration in the double layer region is denoted by DL_i and given by:

$$DL_i = Qz \frac{S_i}{S^{(z)}} \quad (5)$$

in which, $S^{(z)} = \sum S_i^{z+} \quad (6)$

A priori only the total concentrations C_i^z are known. For instance, for a divalent cation, j , in a solution with several monovalent and divalent anions, A_k^- , A_m^{2-} , the relation is:

$$C_j^{2+} = S_j^{2+} + DL_j + DL_{E,j} + (P^{2-} M^{2+})^0 + (E^{2-} M^{2+})^0 + \left(\sum_k (A_k^- S_j^{2+})^+ + ((A_k^-)_2 S_j^{2+})^0 + (P^- (A_k^- M_j^{2+})^+)^0 + (E^- (A_k^- M_j^{2+})^+)^0 \right) + \sum_m (A_m^{2-} S_j^{2+})^0 \quad (7)$$

The reduction in surface charge density is explicitly taken into account according to Equations (1) to (4). The computational procedure is an iterative process based on Equations (1) to (7), using the Gouy-Chapman equation for the surface charge density.

This procedure is described in Nir (18). Briefly, we start from given values for the

binding coefficients and an initial guess for S^+ , S^{2+} , P^- , E^- and the corresponding surface potentials. Then the quantities S_i^+ , S_j^{2+} are calculated and used for the calculations of new values of P^- , E^- and surface potentials. The process is iterated until convergence is attained.

The binding coefficients of Na^+ and K^+ to montmorillonite were taken from Nir et al. (24) and those of Ca^{2+} and Mg^{2+} were taken from Rytwo et al. (25). The association constants of the soluble complexes were taken from Lindsay (26). Based on the results in refs. 25-27, all other association constants could be ignored in the range of cation concentrations (Cu, Ca, Mg) used in our study.

The required parameters were the binding coefficients $K_{2,Cu}$ and H^+ for the edge and planar sites, and those of $(CuCl)^+$.

The study was designed to enable a sequential determination of the parameters, as will be elaborated in the Results section. Each binding coefficient was determined by varying its value until the best fit was obtained between calculated and experimental results, the criteria being the maximization of R^2 and minimization of the root mean square error.

Results and Discussion

Adsorption of Cu on montmorillonite in $NaClO_4$ solutions. Effect of ionic strength.

We first considered adsorption of Cu on montmorillonite in the presence of the inert anion ClO_4^- . Adsorption isotherms of Cu on montmorillonite when $NaClO_4$ was the background electrolyte are plotted in Figure 1. Cu adsorption was dramatically reduced by more than 3.5-fold when increasing the ionic strength up to two orders of magnitude. However, at high ionic strength ($I \geq 0.5$ M), Cu adsorption on the clay mineral surface is independent of the ionic strength used, being the same in the

presence of 0.5 or 1.0 M electrolyte. At low ionic strength the amount of Cu adsorbed increased with its added amounts, but at high ionic strength the adsorbed amounts reach a plateau at 24 mmol/kg clay. This outcome indicates that in the presence of high ionic strength the adsorption of Cu occurs mostly, or exclusively, on high affinity sites of montmorillonite, whose amount is 48 mmol/kg clay. This conclusion was reached by the observation of a plateau and its independence of the ionic strength in a certain range of Cu concentrations. We introduce an assumption that the high affinity sites for Cu adsorption are the edge sites of montmorillonite. Accordingly we performed model calculations in which we introduced a single binding coefficient, $K_{2E, Cu}$ (Eq. 3) for the adsorption of Cu^{2+} on the edge sites. For the determination of this binding coefficient we considered all of the data points in Figure 1 corresponding to the high ionic strengths, whereas for the low ionic strength only Cu^{2+} concentrations below 24 $\mu\text{mol/g}$ were considered, in order to avoid a contribution from Cu^{2+} adsorption on the planar sites of the clay mineral. Thus we had 12 data points to fix this binding coefficient. By considering the enhancement in cation concentrations near the surface (i.e., employing the adsorption model equations) we deduced a value of $2 \times 10^4 \text{ M}^{-1}$ for $K_{2E, Cu}$, whereas by ignoring this effect, a Langmuir equation yielded a value of $7 \times 10^4 \text{ M}^{-1}$. The high binding coefficient calculated for Cu adsorption on the edge sites suggests the formation of inner sphere complexes. High values of binding coefficients have also been reported for formation of inner-sphere complexes of dyes on montmorillonite (19, 23). In these calculations we assumed that the binding coefficients for Ca^{2+} , Mg^{2+} , Na^+ and K^+ binding to the edge sites were the same as previously used by ignoring site heterogeneity. Of course, this is a crude approximation, but it was adequate to explain the adsorbed amounts of all cations in the system, as will be elaborated later.

At low ionic strength Cu adsorption on the clay mineral is taking place onto both interlayer and edge sites, but an increase in the ionic strength will supply more Na^+ ions from the background electrolyte which compete with the heavy metal for the adsorbing sites on the clay, especially for the planar sites which are considered of lower affinity. At 0.5 M NaClO_4 the adsorption of copper on the interlayer sites would be mostly eliminated and the adsorption will mostly occur on the high affinity edge sites. Schindler et al. (15) who studied the effect of the ionic strength on Cu adsorption onto kaolinite obtained that NaClO_4 suppressed the ionic interchange up to pH 4.5, whereas at higher pH values it did not inhibit the adsorption of the heavy metal. Similarly, Zachara et al. (28) noted that, an analysis of the Vanselow coefficients indicated that the adsorption of the heavy metal Cd on planar sites of Na-montmorillonite was eliminated at 0.1 M ionic strength.

The value deduced from Cu adsorption of the CEC of the edge sites from Figure 1 is in a sense an estimate, since Cu adsorption on planar sites also exists, albeit to a significantly smaller extent. This value is close to that observed for collapsed Li-montmorillonite (20.4 mmol/kg) (9, 11). Zachara and McKinley (11) reported a similar value of 22.4 mmol/kg for the amount of aluminol sites on the edge positions, computed from the mean particle diameter, the structural formula and the crystallographic dimensions. When trying to fit Cd adsorption on smectites, the complexation to the silanol groups on the edge sites was calculated to be unimportant (29). We did not establish any distinction between aluminol and silanol sites on the edge positions, but our estimated value for the edge sites concentration can indicate that our modeling is only considering adsorption on aluminol sites.

In the next stage we have determined the binding coefficient of Cu^{2+} to the planar sites of montmorillonite, $K_{2, \text{Cu}}$, from additional 6 data points. The results also

included predictions for the amounts of Ca and Mg remaining adsorbed. In these calculations we considered simultaneous adsorption of all the cations to both planar and edge sites. In the calculations we employed the binding coefficients from previous studies for adsorption of Ca, Mg and Na on the planar sites, and $K_{2E, Cu} = 2 \times 10^4 \text{ M}^{-1}$. Table 1 shows that the model predictions are reasonably good for all the measured adsorbed amounts of the cations at the different ionic strengths used, by employing $K_{2, Cu} = 8 \text{ M}^{-1}$ for Cu binding to the planar positions. At high total Cu concentrations, the decrease observed in the fraction of Cu adsorbed, upon increasing the ionic strength, is adequately explained in the model by a competition with sodium ions for occupancy of the planar sites, together with a decrease in the magnitude of the surface potential, which would reduce Cu binding and its accumulation in the double layer region. However, for the lowest total Cu^{2+} concentrations the percentages of Cu adsorbed are almost independent of the ionic strength used. For these cases, our calculations indicate that Cu^{2+} is almost exclusively adsorbed ($\geq 98\%$) on the edge sites until reaching a value close to their saturation.

We tried to fit the binding coefficient of the proton for each of the two sites. The set of binding coefficients which gave an overall best fit of pH with the experimental values (Table 2) were 10 M^{-1} for $K_{1,H}$ and 18000 M^{-1} for $K_{1E,H}$. Ignoring proton binding produces only a slight variation in the calculated amount of Cu adsorbed ($<1.2\%$), which is due to the much smaller initial amount of H^+ in comparison to the other cations present in the system.

Figure 2 shows the activity of Cu as a function of the pH, calculated using Davies activity coefficients. The points represent the experimental values, whereas the full line was calculated on the basis of the solubilities of the corresponding oxides, hydroxides and carbonates (26). Almost all the observed activities of Cu (II) in the

equilibrium solution were lower than the line representing precipitation, indicating that the concentrations of the metal in solution are controlled by adsorption/desorption reactions and not by precipitation/dissolution processes. Precipitation as $\text{Cu}(\text{OH})_2^0$ could be occurring only for the lowest Cu concentration used at 0.5 M ionic strength (the last point of the right in Fig. 2). In order to test whether precipitation or adsorption occur, we decreased the pH for the two lowest initial Cu concentrations at 0.5 M NaClO_4 , by adding aliquots of 0.1 M HCl. The experimental values of Cu adsorbed obtained were 98.6 and 85.1% at added concentrations of 40.1 and 86.5 μM , respectively. This is in very good agreement with the calculated values, which are 98.3 and 85.0%, respectively. At lower pHs there is not precipitation of $\text{Cu}(\text{OH})_2^0$, thus, the decrease of Cu in the equilibrium solution can be ascribed only to adsorption processes. Since lowering of the pH only modified slightly the experimental percents of Cu adsorbed, we may deduce that even at the higher pH the main process is adsorption and not precipitation. The high percents adsorbed are due to the high affinity of Cu^{2+} for adsorption on the edge sites in comparison to that of other cations.

The equilibrium pH decreases as long as copper adsorption proceeds at any fixed ionic strength (Tables 1, 2). This decrease in the equilibrium pH is not only attributed to its lower initial pH with increasing its total concentration, due to the lack of a constant value in the pH increments. The release of protons observed may be associated with exchange reactions at the surface, metal hydrolysis in solution or at the surface, hydrolysis of the adsorbent surface, or a combination of these (30). These equilibria can be simplified for the metal in solution, that can be considered as mostly Cu^{2+} , according to the hydrolysis constants given by Lindsay (26), except for the lowest initial Cu concentrations where the pH is higher. Indeed, the modelling of formation of CuOH^+ in solution and its adsorption hardly modified the calculated

equilibrium pH (values not shown). We did not consider hydrolysis of the metal in the surface since there is no conclusive spectral evidence on smectites (31).

Effect of Cl^- on Cu adsorption

The introduction of the chloride anion instead of the perchlorate anion reduces the amount of Cu adsorbed on the clay, due to the complexation reaction between copper and chloride (Table 3). The effect of Cl^- on Cu adsorption on the clay at the lowest ionic strength is minimal, amounting to a reduction by less than 10%. In the presence of 1.0 M NaCl the largest adsorbed amounts of Cu are about 18 mmol/kg. The major complexation reactions in solution between Cu^{2+} and Cl^- produce CuCl^+ and CuCl_2^0 , whose concentrations increase with an increase of the ionic strength according to their association constants given by Lindsay (26), $10^{0.5} \text{ M}^{-1}$ and $10^{-0.12} \text{ M}^{-2}$, respectively. The adsorption of the neutral species CuCl_2^0 was ignored.

The binding coefficient of CuCl^+ could be determined by 15 data points (Table 3). We used the same value of the binding coefficient (20 M^{-1}) for both the planar and edge sites. The calculated adsorbed amounts of total Cu agree reasonably well with the experimental results (Table 3). Table 3 also shows that for the lowest ionic strength the fraction adsorbed as the monovalent cation CuCl^+ is negligible, becoming relatively important only for the highest ionic strength. These results are consistent with those reported by Zhang and Sparks (32) who reached the conclusion that CuCl^+ did not adsorb on montmorillonite for Na-Cu exchange. The Cl^- concentration they used was 0.02 M, for which our model predicts almost no adsorption of Cu complexes.

According to the calculated speciation of Cu adsorbed in Table 3, the interchange between Cu and the interlayer sites is not zero even in the presence of 1 M

NaCl. The results in Table 3 indicate that under this condition a great deal of the amount adsorbed on the planar sites arises from the CuCl^+ species. The largest calculated adsorbed amount on the edge sites is 20.1 mmol/kg, whereas in NaClO_4 the corresponding value was 24 mmol/kg.

In Table 4 we present additional results of copper adsorption by using a background electrolyte solution of 10 mM NaCl and added KCl or CsCl at concentrations of 0.5, 5.0 and 10.0 mM. These added results were mainly introduced to test the ability of the model to yield predictions for cases not included in the determination of the parameters, such as electrolytes rich in K or Cs. According to previous results (24), the effect of K^+ on the reduction of the percentage of copper adsorbed should be larger than that of Na^+ and the effect of Cs^+ is expected to be much larger. Overall the predictions are quite good ($R^2 = 0.96$; RMSE= 4.2%) despite using for Ca^{2+} -montmorillonite binding coefficients determined for Na^+ -montmorillonite. The results in Table 4 also indicate that K^+ or Cs^+ do not exhibit a very large binding affinity to the edge sites of Ca-montmorillonite.

Desorption of Cu preadsorbed on montmorillonite

Adsorption-desorption isotherms of Cu on the clay mineral surface at 0.01 M NaCl are plotted in Figure 3. The desorption isotherms exhibit an apparent hysteresis, that is, more Cu remains adsorbed than would be expected according to the adsorption cycle. Prolongation of incubation time to two weeks did not increase the released amounts of Cu. However, the model yields good predictions for the adsorbed amounts of Cu (as well as Ca and Mg, data not shown) in all the adsorption-desorption cycles (Table 5). In this table, data corresponding to adsorption-desorption points at 0.1 M NaCl have also been included.

Inspection of Tables 3 and 5 indicates that when the adsorbed amounts of Cu are mainly due to its adsorption on the edge sites, the fractions of Cu adsorbed are close to unity. This is due to the large binding affinity of Cu^{2+} to the edge sites. Thus, the released amounts of Cu in the desorption cycles are largely from the planar sites.

Table 5 illustrates that the calculated fractions of Cu adsorbed on the planar sites decrease throughout the desorption cycles. This effect is more pronounced in the case of the highest total Cu concentration used (487.2 μM) at 0.1 M NaCl. Our calculations indicate that there is almost no desorption from the edge sites for the highest Cu concentration used, whereas the desorption from the edges sites is very small for the lowest Cu concentration used.

The hysteresis arising from planar sites as observed for the highest Cu concentration added in 0.01 M NaCl can be mostly explained by the fact that the desorption cycles involve centrifugation, removal of the half of the supernatant and addition of a corresponding volume of 10 mM NaCl, and thus the total concentrations of Ca and Mg which affect Cu adsorption due to competition are reduced. Part of this effect is due to a small increase in the magnitude of the surface potential due to a smaller sum of total concentrations of divalent cations in desorption cycles, which results in higher Cu^{2+} or CuCl^+ concentrations at the surface according to Eq. (4). Indeed, when supplementing the amounts of Ca and Mg desorbed in the adsorption stage for the first desorption step the amount of Cu desorbed increases and the hysteresis is largely reduced. Calculations also indicate that some degree of hysteresis would also occur with Na-montmorillonite (18). The hysteresis also decreased largely when the same procedure of supplementing the removed Ca^{2+} and Mg^{2+} was applied at 0.1 M NaCl for the largest Cu concentration (results not shown).

Concluding Remarks

In the current study the determination of the binding coefficients of Cu on montmorillonite was facilitated by the ability to design experiments which enabled their sequential determination. Thus the use of high concentrations of NaClO₄ (0.5 and 1.0 M) permitted to account for the adsorption of Cu²⁺ to the edge sites. In fact, the calculations which take into account adsorption on both sites (Table 1) indicate that at the plateau (Figure 1) the total amount of Cu adsorbed on the edge sites amounts to 24 mmol/kg.

The adsorption model could explain and predict all the sets of copper adsorption results for 20-fold variation in its total concentrations and for two orders of magnitude variation in ionic strengths. Similarly, we demonstrated the ability of the model to predict the adsorbed amounts of copper upon an order of magnitude variation in K⁺ or Cs⁺ concentrations.

The ability of our model to yield predictions by using only one set of binding coefficients for describing Cu adsorption on montmorillonite for all the range of ionic strengths used, is an advantage in comparison with other applied models, such as the constant capacitance model used by Stadler and Schindler (16). In this model, simple proportionality relations are used between the surface potential and the charge density, with no explicit consideration of the effect of the background electrolyte. Therefore all the parameters obtained should be considered for comparison at the same ionic strength. McBride (33) reported examples where complex models are used to explain chemical adsorption that often has a simpler explanation. In this line, Hayes et al. (34) when trying to fit the potentiometric titration of an oxide, reached the conclusion that it was much better to use a diffuse double layer model in spite of not being able to fit the experimental data as precisely as the triple layer or constant capacitance models.

This was due to its simplicity together with its capacity to reach a single set of parameters. The advantage of our model is both in its agreement with observations to the extent of yielding predictions, and simplicity.

Model calculations also enabled us to predict the outcome of desorption cycles and explain quantitatively the hysteresis observed. The hysteresis arises from the heterogeneity of sites and is not due to either kinetic effects or changes in the chemical nature of the adsorbed metal following adsorption. The contribution of planar sites to hysteresis is a function of equilibrium partitioning whereas in the case of the edge sites, the adsorption is almost irreversible due to the large affinity of the heavy metal for these positions. The calculations also enabled to elucidate the contribution of the edge sites to Cu adsorption, and provide estimates for Cu adsorption as Cu^{2+} vs. CuCl^+ in chloride solutions.

Our study illustrates that it is risky to extrapolate the mobilization potential of Cu, and perhaps other heavy metals. Up to certain levels of copper, soils rich in clays can retain the heavy metal, but at higher added amounts and, in particular at higher ionic strengths, copper may be mobilized.

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Figure Captions

Figure 1. Adsorption isotherms of copper on montmorillonite at several ionic strengths (I) when using NaClO₄ as background electrolyte.

Figure 2. Copper activity in equilibrium solutions versus pH. The ionic strength was 0.5 N NaClO₄. The activity coefficients were calculated by using Davies equation. The solid line indicates formation of Cu(OH)₂⁰ (s).

Figure 3. Adsorption-desorption isotherms of copper on montmorillonite. The ionic strength used was 0.01 M NaCl.

Table 1. Percentages of Cu, Ca and Mg adsorbed on montmorillonite as a function of the ionic strength and the amount of Cu added. Experimental and calculated values. The background electrolyte used was NaClO₄. ^{†,‡}

Ionic strength (M)	Cu added (μM)	Cu (%)		Ca (%)		Mg (%)	
		Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.01	31.0	99.3	99.7	86.7	83.7	84.2	81.0
	63.7	98.4	99.5	86.2	83.0	83.4	80.3
	152.0	97.1	94.2	84.7	81.3	81.6	78.4
	239.0	95.1	87.9	83.0	78.8	80.0	76.8
	329.0	91.3	83.9	81.6	78.4	78.2	75.2
	516.0	85.4	78.7	78.4	75.4	74.3	72.0
0.5	31.5	97.6	94.2	13.4	10.2	11.6	8.5
	63.9	91.8	90.2	15.3	9.9	11.2	8.2
	143.0	74.1	68.4	15.3	9.6	11.4	7.9
	226.0	47.6	50.0	15.8	9.5	10.9	7.9
	300.0	37.0	40.7	15.7	9.5	10.3	7.9
	461.0	29.9	35.1	15.5	9.4	9.4	7.8
1.0	37.4	95.3	85.5	6.2	4.3	9.0	3.5
	148.0	62.2	58.1	3.1	4.1	7.5	3.3
	236.0	47.4	43.8	4.2	4.0	8.7	3.3
	310.0	38.9	34.6	4.6	4.1	8.7	3.3
	459.0	25.4	25.5	4.8	4.2	9.3	3.3

[†]. The calculations employed the following values of binding coefficients for planar sites: Cu (8 M⁻¹) (current work); Ca (10 M⁻¹), Mg (8 M⁻¹) as in Undabeytia et al. (20) and Rytwo et al. (25); Na (1 M⁻¹); H (10 M⁻¹) (current work) and K (4 M⁻¹) as in Nir et al. (24). For the edge sites the same binding coefficients were used, except for copper and the proton, for which a binding coefficient of 2x10⁴ M⁻¹ and 1.8x10⁴ M⁻¹, respectively, were used. The total concentrations in the system (clay + solution) were 2.52 mM for Ca, 0.479 mM for Mg, and 0.048 mM for K (Na concentration varied with the ionic strength used).

[‡]. The relative standard deviations obtained for Cu adsorption ranged between 0.1 and 5.0 %.

Table 2. Calculated and measured pH for Cu adsorption as a function of its amount added at high ionic strengths in NaClO₄ media. The variation between the pH of the final and initial Cu solutions (Δ pH) is also shown.

Ionic strength (M)	Amount added (mmol/kg)	Measured pH	Calculated pH	Δ pH
0.5	6.30	7.83	7.45	1.08
	6.30	6.54*	6.55	0.66
	12.78	6.97	7.22	0.33
	12.78	6.19*	6.08	0.60
	28.66	6.19	6.47	0.05
	45.31	5.90	5.83	0.29
	60.15	5.72	5.73	0.18
	92.39	5.67	5.73	0.08
1.0	7.49	6.92	6.71	0.74
	12.13	6.55	6.46	0.54
	29.70	6.07	6.21	0.15
	47.35	5.92	6.06	0.12
	62.02	5.76	5.85	0.08
	91.99	5.73	5.76	0.10

*Adjusted initial pH.

Table 3. Percentages of Cu adsorbed on different sites of montmorillonite as a function of the ionic strength and the amount of Cu added. The background electrolyte used was NaCl.[†]

Ionic strength (M)	Cu added (μM)	Cu (%)		Cu^{2+}		CuCl^+	
		Exp	Calc	(planar) [‡]	(edge) [‡]	(planar) [‡]	(edge) [‡]
0.01	81.1	95.3	99.2	3.1	96.9	<0.1	<0.1
	161.2	91.6	93.2	25.6	74.4	0.1	<0.1
	244.1	88.0	87.4	45.9	53.8	0.3	<0.1
	327.7	84.9	83.6	57.4	42.2	0.4	<0.1
	412.8	82.6	80.8	64.7	34.9	0.4	<0.1
	489.1	80.0	78.6	69.2	30.3	0.5	<0.1
0.1	80.7	92.9	95.5	2.1	97.6	0.3	<0.1
	162.9	78.2	76.8	13.1	84.9	2.1	<0.1
	237.6	70.2	63.6	24.1	72.1	3.8	<0.1
	335.6	64.6	56.3	34.4	60.1	5.5	<0.1
	496.5	54.0	46.3	45.2	47.5	7.3	<0.1
1.0	146.0	49.9	44.4	1.1	92.2	6.5	0.1
	252.0	41.3	35.4	1.8	87.6	10.4	0.2
	295.5	31.1	28.8	2.0	85.9	11.9	0.2
	453.2	22.4	21.0	2.9	79.9	17.1	0.2

[†]. See Table 1 for the binding coefficients used. The binding coefficient used for CuCl^+ adsorption on both planar and edge sites was 20 M^{-1} .

[‡]. The calculated speciation percentages are relative to the total amount of Cu adsorbed. The relative standard deviations obtained for Cu adsorption ranged between 0.1 and 2.3%.

Table 4. Percentages of Cu adsorbed on montmorillonite in the presence of 10 mM NaCl and several KCl or CsCl concentrations. Experimental and calculated values.^a

Electrolyte added (mM)	Conc. added (mM)	Cu added (μ M)	Cu (%)	
			Exp.	Calc.
KCl	0.5	52.6	97.1	99.5
		497.1	80.6	78.4
	5.0	56.3	95.8	99.3
		480.1	72.0	73.4
	10.0	44.9	93.3	99.2
		483.7	62.0	68.3
CsCl	0.5	66.8	98.3	99.3
		478.1	80.7	75.7
	5.0	59.1	97.2	96.7
		436.1	44.8	49.6
	10.0	61.7	95.1	90.0
		428.5	29.7	36.1

- a. The relative standard deviations obtained for Cu adsorption ranged between 0.1 and 2.0% for the case of KCl and between 0.01 and 6.5% for CsCl. The calculations give $R^2 = 0.96$ and RMSE= 4.2%.

Table 5. Percentages of Cu adsorbed on montmorillonite sites and its speciation in adsorption-desorption cycles as a function of ionic strength and the amount of Cu added.[†]

Ionic strength (M)	Cu added (μM)	Step	Cu adsorbed (%) [‡]		Distribution of Cu adsorbed (%)		
			Exp	Calc	planar	edge	CuCl^+
0.01	81.1	Ads.	95.3	99.2	3.1	96.9	-
		Des. #1	96.1	99.5	2.8	97.2	-
		Des. #2	96.8	99.6	2.7	97.3	-
		Des. #3	96.9	99.7	2.6	97.4	-
0.01	161.2	Ads.	91.6	93.2	25.6	74.4	0.1
		Des. #1	94.6	95.3	23.5	76.4	0.1
		Des. #2	95.4	96.4	22.5	77.5	-
		Des. #3	96.0	97.2	21.5	78.5	-
0.01	489.1	Ads.	79.9	78.9	69.0	30.5	0.5
		Des. #1	87.1	84.9	68.2	31.4	0.4
		Des. #2	90.7	88.4	67.5	32.2	0.3
		Des. #3	92.7	90.5	66.8	32.9	0.3
0.1	75.2	Ads.	91.4	96.2	1.8	97.9	0.3
		Des. #1	94.7	97.4	1.6	98.2	0.2
		Des. #2	96.8	98.1	1.4	98.4	0.2
		Des. #3	98.3	98.6	1.2	98.7	0.1
0.1	487.2	Ads.	50.1	49.0	44.4	48.0	7.2
		Des.#1	62.7	58.4	40.3	54.0	5.7
		Des.#2	71.2	65.6	36.8	58.4	4.8
		Des. #3	79.2	72.1	32.2	64.0	3.8

[†]. The percentages are expressed with respect to the total amounts (adsorbed + in solution) for each step. See Tables 1 and 3 for the binding coefficients used. The background electrolyte used was NaCl.

‡. The relative standard deviations obtained for Cu adsorption ranged between 0.1 and 2.3%.

Figure 1

Figure 2

Figure 3