

ADSORPTION OF Cu IONS ONTO A 1.10 PHENANTHROLINE-GRAFTED BRAZILIAN BENTONITE

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Abstract—The grafting, by chemical adsorption, of molecular 1.10-phenanthroline (OP) onto some Brazilian bentonite (montmorillonites) was studied to improve their adsorptive capacities to remove Cu ions from synthetic wastewater. The quantity of OP adsorbed was 112 mg g⁻¹ of bentonite at pH 8.5 and no significant desorption was detectable in acidic or basic solutions. X-ray diffraction (XRD) spectra show that a complex type-β is formed in which the OP molecules lay inclined in the clay interlayer. After the intercalation of OP, the adsorptive capacities of the natural bentonites increased by a factor of ten. Thus, adsorption of Cu ions, at optimal pH of 8.0±0.5, showed saturation values, which, calculated by the Langmuir model, yielded 110 mg of Cu ions g⁻¹ of bentonite (3.5 meq g⁻¹). The mechanisms of Cu uptake are ion-exchange adsorption onto untreated bentonite and ion exchange plus Cu²⁺ phenanthroline complexation (chemisorption) on the modified pillared clay. The desorption of Cu ions from OP clay revealed high uptake irreversibility and physical stability (of the adsorbent) either in strongly acidic or basic solutions. Thus, after acid treatment ~90% of the adsorbed Cu ions continued to be bound onto the OP-modified bentonite surface.

Key Words—Adsorption, Bentonite, Delaminated, Intercalation, 1.10 Phenanthroline, Pillared.

INTRODUCTION

The accumulation of heavy metals by modified and natural bentonite particles in contaminated liquid effluents attracts considerable interest in the fields of soil science and industrial wastewater treatment. Significant amounts of heavy metals can accumulate in soils, soil organisms, plants and in surface- and groundwaters, sometimes causing severe environmental problems. The adsorption of contaminants using several possible (and cheap), adsorbents has recently been investigated and used in wastewater treatments (Costa *et al.*, 1999; Rubio and Tessele, 1997; Féris *et al.*, 2001; Bailey *et al.*, 1999).

Bentonite is a clay that usually occurs as smectite crystals of colloidal size. Its parallel and stacked silicate layers are, according to Souza de Santos (1975) and De Queiroz (1977), ~10 Å thick. These layers are negatively charged because of ionic substitutions at various sites within their structures and, as a result, exchangeable cations are 'adsorbed' on their surfaces (Lagaly, 1981).

Smectite clays play important roles in a variety of waste management and treatment strategies. For example, the smectites are often compacted and used as liners in landfills, in bentonite slurry walls and in other waste-containment systems (Anderson *et al.*, 1999). Yet, despite having a relatively large cation exchange capacity (CEC), the lack of selectivity sometimes limits their application. In environmental studies, bentonites may be modified to enhance their reactivity toward more

specific contaminants. Thus, the surfaces of some bentonites have been modified either by the addition of alkyl cations to change the polarity and hydrophobic character of the surface and thereby enhance retention of organic pollutants (Mortland *et al.*, 1986; Srinivasah and Fogler, 1990) or by intercalation of some organic "extractants" to remove heavy metals from aqueous solutions (Appleton *et al.*, 1999). Moreover, it has been demonstrated by several researchers (Clementz and Mortland, 1974; Mortland and Berkheiser, 1976) that amines react chemically with bentonites to form organo-clay complexes known as pillared smectites.

The present work was undertaken with the aim of examining the influence of OP intercalation into a Brazilian bentonite on adsorptive capacities for metal ions from aqueous solutions. Other objectives were to measure the physical and chemical stability of the modified bentonite and to present results of the physical and technological characterization of this modified bentonite.

In this work, the term delaminated is used to identify a Na-saturated clay and the OP-treated clay is referred to as pillared clay.

EXPERIMENTAL

Materials

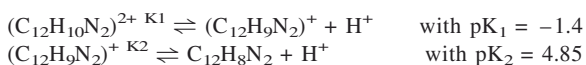
Bentonite. The raw clay used was an industrial treated Na⁺-montmorillonite, from Campina Grande, Paraíba, Brazil. This clay had a CEC of 0.80 meq g⁻¹ and specific surface area of 696 m²g⁻¹ measured using the methylene blue adsorption method, described by Hang and Brindley (1970). A commercial sample was screened and particles <74 μm were used throughout.

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Phenanthroline. The 1.10 phenanthroline (OP) ($C_{12}H_8N_2 \cdot H_2O$), from Synth (Brazil) is of analytical grade; it has a molecular weight 198.22 g and a water solubility of 3.3 g L^{-1} . According to Brinen *et al.* (1963), OP would dissociate as follows:



The OP concentrations were determined by a colorimetric method described by Lawrie (1961); the reaction color was developed with ferrous iron in the presence of hydroxylamine hydrochloride, a reducing agent, and the optical measurements were made in 16 mm cells at a wavelength of $510 \mu\text{m}$ (Photometer MERCK SQ 118) with acetate buffer.

Preparation of homoionic clays

The preparation of homoionic clays was conducted by suspending Na^+ -bentonites in deionized water in a 1:60 clay:water ratio, containing 3 meq of the substituting cation (Ca^{2+} in the chloride form) per gram of clay. The suspension was stirred continuously for 48 h at room temperature, separated from water by centrifugation, and washed free of excess ions with deionized water, until a negative silver nitrate test was obtained. The solid materials, Ca-saturated clay, were dried at 60°C for 48 h, disaggregated and stored at room temperature.

Intercalation of the homoionic clays

The intercalation of OP into the homoionic clays was effected by adding the reagent at a concentration of 150 mg g^{-1} of clay, dissolved in a binary solvent of 1:1 ethanol-deionized water. A liquid:solid ratio of 40:1 was used to ensure complete dispersion, and the Pyrex bottles were then shaken for 1 h at room temperature, at different pH, by adding HCl or NaOH. Then, samples were centrifuged at 3382 g for 10 min (SIGMA 2k15) and the supernatant solutions were analyzed for OP concentrations. The amount of OP adsorbed by the bentonite was determined by the difference between initial and final concentrations. The Ca released from the homoionic clays was measured by flame atomic absorption spectroscopy (SpectrAA 110-Varian). In the intercalation studies, 12.5 g of homoionic bentonite were mixed with a solution of the intercalation reagent (1.875 g of OP) dissolved in a binary solvent (500 mL) of 1:1 ethanol-deionized water. The resulting pillared clay was oven dried for 12 h at 60°C , disaggregated, dried again for 24 h at 60°C , and finally stored at room temperature.

Adsorption studies

Adsorption studies of Cu ions onto bentonites, modified or not, were conducted using the following procedure (Schneider *et al.*, 1999, 2001; Féris, 2001; Féris *et al.*, 2001): 0.1 g of adsorbent was suspended in a pH 3 solution in glass bottles (capacity of $\sim 100 \text{ mL}$).

Then, 0.63 mL of a $CuSO_4$ of 1000 mg L^{-1} solution (pH 2) were added to yield a constant concentration of 6.3 mg L^{-1} ($1 \times 10^{-4} \text{ M}$). Finally, medium pH was adjusted to the desired value and the glass bottles shaken in an orbital device at 55 rpm at room temperature. This method ensures no precipitation of $Cu(OH)_2$ because the Cu equilibrium solution concentration, (considering progressive adsorption), was always less than that needed to attain the K of $Cu(OH)_2$ precipitation. The pH of extraction was varied by the addition of either NaOH or HNO_3 solutions. Then, equilibrated clays and solutions were separated by centrifugation (6289 g for using a SIGMA 2k15), and the supernatant solutions were analyzed by flame atomic absorption spectroscopy (SpectrAA 110-Varian). The amount of Cu adsorbed and its accumulation were calculated as follows:

$$R = (C_i - C_f) * 100 / C_i \quad (1)$$

$$A_c = (C_i - C_f) / M \quad (2)$$

where R = Cu removal (%); C_i = initial aqueous concentration (mg L^{-1}); C_f = final aqueous concentration (mg L^{-1}); A_c = mass of solute adsorbed per unit weight of adsorbent (mg g^{-1}); M = adsorbent/solution concentration (mg L^{-1}).

Kinetics experiments indicated that equilibrium was attained in 10–30 min, thus 1 h contact time was selected to ensure that equilibrium was reached.

The isotherms were measured at 25°C , at pH 8.5, by equilibrating known fixed amounts of clays in standardized solutions containing different concentrations of Cu ions. To avoid an eventual Cu precipitation – before the adsorption – by the increase of its concentrations and pH values, aliquots of 0.25 mL (to yield 2.5 mg L^{-1} as total concentration) were added to the clay suspension during the adsorption time (initiating at pH of ~ 3). The adsorption of Cu ions on the pillared and delaminated bentonite was analyzed using a double reciprocal plot based on a Langmuir-type adsorption equation:

$$1/A_c = 1/a + 1/a * b * C_e \quad (3)$$

where A_c = mass of solute adsorbed per unit weight of adsorbent (mg g^{-1}); C_e = concentration in solution at equilibrium (mg L^{-1}); a = adsorption capacity (mg g^{-1}); and b = adsorption equilibrium constant (L mg^{-1}). When C_e/A_c is plotted against C_e , a linear isotherm is obtained. The constant b is obtained by dividing the slope of the isotherm by its intercept, and the quantity a is the reciprocal of the slope of the isotherm.

The adsorption isotherms were plotted as a function of the equilibrium solution concentrations and the amount of Cu^{2+} adsorbed, expressed in meq g^{-1} of adsorbent.

Reversibility and desorption experiments

(1) The reversibility of the OP adsorbed into the homoionic clays was studied after its intercalation with

three solutions of different concentrations, by resuspending pillared clay in mixtures of fresh leaching solutions (Comans, 1987), namely: tap water, HCl, 2% v/v and NaOH, 0.2 M. A solid:liquid ratio of 1:50 was employed, suspended under stirring for 2 h, and then separated by centrifugation of the suspension (3382 g for 10 min SIGMA 2k15). Finally, the supernatant solutions were analyzed for OP released.

(2) The desorption experiments of Cu ions adsorbed onto pillared clay was performed in batch tests at room temperature by adding to a dried (at 60°C overnight) loaded adsorbent, a leaching solution (HCl by 2% v/v at pH 1±0.2) with a solid:liquid ratio of 1:500 suspended under stirring for 2 h, followed by centrifugation (6289 g for 20 min using a SIGMA 2k15). At the end of the leaching period, an aliquot of the supernatant solution was analyzed to determine the amount of Cu ions released.

Three-step sequential adsorption:desorption runs were conducted to determine the mobilization factor (Rybicka *et al.*, 1995) in each experiment, following the equation:

$$K_{SD} = M_{ads}/M_{des} \quad (4)$$

where K_{SD} = the adsorption:desorption ratio; M_{ads} = the amount of solute adsorbed (mg g^{-1}); M_{des} = the amount of solute desorbed (mg g^{-1}).

All experiments were repeated twice and the reported values correspond to the mean values; the coefficient of variation was ~5%.

X-ray studies

The extent of interlayer adsorption of OP by Brazilian bentonite was characterized by determining the major basal spacing of OP-treated and untreated samples by XRD. The clay samples for XRD were prepared by packing air-dried powder on glass slides. For the XRD a Siemens Kristalloflex D5000 powder diffractometer using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.542 \text{ \AA}$) was used.

RESULTS AND DISCUSSION

The XRD analysis showed that this bentonite sample is rich in montmorillonite showing a symmetric peak,

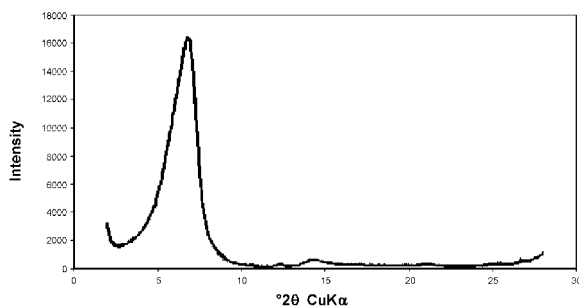


Figure 1. X-ray powder diffraction pattern of Na-bentonite showing minor peaks for kaolinite and quartz.

which indicates a layer spacing of 12.9 Å (Figure 1). Associated minerals such as quartz and kaolinite were found to be present.

OP intercalation

The effect of pH on OP grafting on bentonite was measured in the equilibrium pH range 3.5 to 8.5. The amount of OP adsorbed and the basal spacings are listed in Table 1. The data show a maximum OP adsorption of (121 mg g^{-1}) at pH 5.5 ± 0.5 . According to De Bussetti *et al.* (1980), at this pH value >90% of the OP molecules are in the uncharged form. This fact appears to indicate that the uncharged form is preferred over the positive species and that the OP is adsorbed, at the bentonite/solution interface, as a micellar unit. A slight decrease in OP adsorption above pH 6 was also reported by De Bussetti *et al.* (1980).

The basal spacing of the OP-pillared bentonite did not change significantly upon pillaring, indicating the existence of a β -type interlamellar formation (Aragon *et al.*, 1959) with an OP molecule lying inclined with respect to the clay layer. As can be seen in Table 1, the expansion of the major basal spacing was ~5.5 Å and is in agreement with Bower (1963), who reported values of the order of 5.3 to 7.8 Å (clay-OP system). Accordingly, if the thickness of one OP molecule is considered to be 3 Å (De Bussetti *et al.*, 1980) and the projected surface area of one OP molecule $\approx 60 \text{ \AA}^2$ (Lawrie, 1961), the other dimensions are of the order of 8 Å (greater length than thickness). Thus, for expansions of ~5.5 Å, we conclude that adsorbed OP lay inclined to the clay surface (Barshad, 1952).

Assuming this orientation, the micelle comes in contact with the two surfaces of the interlamellar spaces of the crystals. The findings reported by Srinivasan and Fogler (1990) are in agreement with this orientation model. Those authors adsorbed cetyl pyridinium ions that were oriented vertically on montmorillonite interlayers. De Bussetti *et al.* (1980), Ferreiro *et al.* (1988) and Helmy *et al.* (1983) reported similar results for quinoline and OP adsorption on other clays and oxides. Yet, these orientation models differ from those reported by Lawrie (1961) in which the OP molecule would lie parallel to the clay layer. Lawrie proposed a method for determining approximately the surface areas of clays

Table 1. Total amount (A_c) of OP adsorbed and major basal spacing of OP-treated and untreated bentonite.

Sample	Intercalation pH	A_c (mg of OP g^{-1})	d_{001} (Å)
Raw clay	–	0	12.9
Ca-saturated clay	–	0	15.0
Pillared clay	3.5	104.0	17.7
	5.5	121.0	18.4
	8.5	112.0	18.2

Table 2. Total amount of OP released and K_{SD} values at the end of reversibility studies.

Leaching solutions	Stage	OP released (mg g ⁻¹)	K_{SD}
Tap water	1	1.3	91.0
	2	1.6	73.3
	3	0.8	144.0
Acidic	1	13.4	8.8
	2	15.0	7.0
	3	14.0	6.4
Basic	1	2.8	41.8
	2	3.8	30.0
	3	3.4	32.1

based on the adsorption of OP, assuming that the planar OP molecule lies flat on the adsorbent. Conversely, Bower (1963) and De Bussetti *et al.* (1980) suggested that the assumption that the amount of OP adsorbed corresponded to a monolayer may not be strictly valid, because the experimental conditions under which the adsorption model of OP was measured can be considered arbitrary. Instead, through the expansion in the interlamellar spacing of bentonite, the OP molecules penetrate readily taking a specific orientation between interlayer surface depending on the OP adsorbed species (Aragón *et al.*, 1959).

Studies of Cu ion adsorption by pillared clay either at pH 5.5±0.5 or 8.5±0.5, showed similar uptake values of the order of 98%. Hence, the pillared clay treated at a basic pH was used throughout the adsorption studies, because this was the natural pH of the aqueous suspensions. The pillared clay has residual, non-grafted sites, because the OP intercalation fulfilled only 80% of the initial CEC capacity. This value was measured by monitoring the quantity of Ca released from the clay surface during the intercalation studies. In addition, because of the difficulties in measuring the area occupied by the inclined OP molecules, a rough estimate would be >12% of the total available area. This calculation was made from a hypothetical vertical orientation at the surface.

The reversibility data of the OP are shown in Table 2. The mobilization factor indicated that OP bound in an interlayer of bentonite is strongly fixed. According to the K_{SD} values, the mobility of OP yields the following average leaching sequence: acid solution >> soda solutions > tap water.

Adsorption studies

The effect of pH on the adsorption of Cu ions on pillared and delaminated bentonites was studied in the pH range 1.5 to 12.5 and the data are shown in Figure 2. The adsorption efficiency of Cu ions by the pillared clay was independent of medium pH. This phenomenon can be explained by complexation of the Cu ions by the anchored OP, *i.e.* chemisorption, which is independent

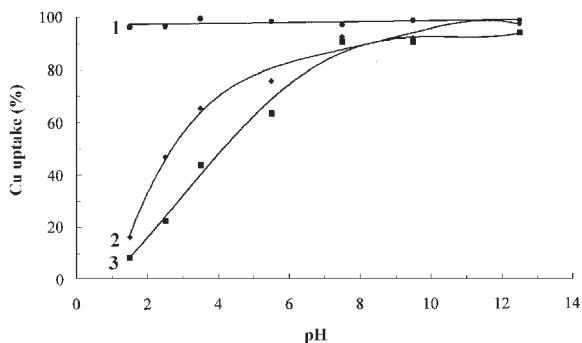


Figure 2. Effect of pH on adsorption of Cu ions onto pillared (1), raw (2) and Ca-saturated (3) clays.

of medium pH. This chemisorption is consistent with the high equilibrium constant (K_2 of 15.82) for the OP-Cu (CuL_2^{2+}) complexes (Sillén and Martell, 1971; James and Williams, 1961).

On the other hand, in the raw clay or Ca-saturated clays, the Cu ion uptake increased when the solution pH was increased from 1.5 to 7.5. Here, cation exchange constitutes the main mechanism responsible for the cation uptake.

For a similar Cu ion concentration (1×10^{-4} M), Chen and Wu (2000), reported that the Cu ion adsorption trend, between pH 2 and 7.5, was similar to our results. Those authors, using MINEQL, a computer program for the calculation of chemical equilibrium composition of aqueous systems, demonstrated that the Cu precipitation reactions did not take place in the investigated solution pH range. Instead, the increase in the uptake of Cu ions was due to ion adsorption and not to $\text{Cu}(\text{OH})_2$ precipitation. The decrease in Cu ion adsorption at lower pH can be explained by H^+ ions present in high concentration which compete with Cu^{2+} ions for the binding sites. As the pH was increased, the Cu ion adsorption efficiency increased as a consequence of ion exchange. Similar results have been found in our laboratory with non-living aquatic plant biomass and coal beneficiation tailings (Schneider *et al.*, 2001; Férís *et al.*, 2001; Costa *et al.*, 1999).

Figure 3 shows adsorption kinetic data collected over 1 h (the equilibrium time). In general, it can be seen that

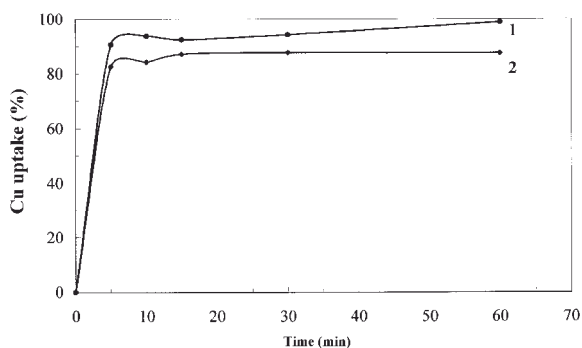


Figure 3. Adsorption of Cu ions on pillared (1) and raw clay (2) as a function of time at pH 8.5.

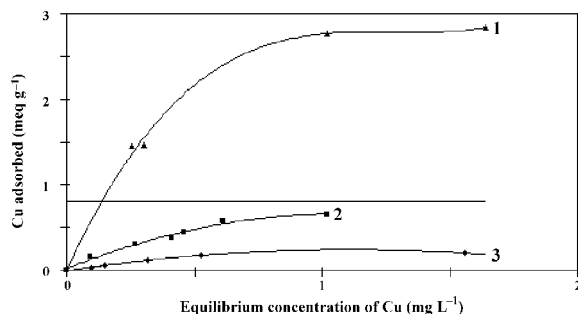


Figure 4. Adsorption isotherms of Cu ions by pillared (1), Ca-saturated (2) and raw (3) clays at pH 8.5. The line at Cu ion adsorption of 0.8 meq g^{-1} corresponds to the CEC value of the bentonite.

for the two adsorbents, a very rapid initial adsorption process occurred within 5 min during which most of the Cu ions were adsorbed and no more uptake was observed after 10 min. The equilibrium time was less than that for the Cu ions adsorption by activated carbon found by Chen and Wu (2000).

Figure 4 shows the experimental data for Cu ion adsorption isotherms for the three adsorbents studied. These figures show that the pillared clay exhibits a marked affinity for Cu ions in aqueous solution. The Cu-pillared clay isotherm cannot be interpreted other than as an exchange adsorption phenomenon because the pillared clay adsorption capacity exceeds the CEC (0.8 meq g^{-1} of bentonite). Thus, the high capacity for Cu ion uptake presented by pillared clay may be caused by it being a binary-site model, where (1) there is adsorption by ionic exchange on fixed-charge sites, on the basal plane and on the edges of the layers silicates, and (2) there are complexation reactions with the OP molecules adsorbed in the interlayer.

It is evident that the OP intercalation greatly influences the adsorption of Cu ions. The surface orientation of the OP adsorbed leads to large areas of

Table 3. Langmuir constants for the adsorption of Cu by pillared, raw and Ca-saturated clays.

Adsorbent	Langmuir constants		
	R^2 *	a mg g^{-1}	B L mg^{-1}
Raw clay	0.90	9.2	1.55
Ca-saturated clay	0.94	24.4	2.56
Pillared clay	0.98	110.0	2.84

* Correlation coefficient

the pillared clay surface being exposed allowing the adsorption of small molecules and may also provide a clue to the high adsorption potential of this new adsorbent.

The Langmuir constants for the adsorption of Cu ions on bentonites and the correlation coefficients are shown in Table 3. The values of the adsorption equilibrium constant b appear to indicate that the differences in the energies of adsorption of the Cu ions by bentonites may be due to the adsorption mechanisms involved.

The Langmuir constant, a , which is indicative of the adsorption capacity, was found to be 110 mg Cu g^{-1} of pillared clay. This value is very high compared to some of the values reported by other researchers for other types of adsorbents (Costa *et al.*, 1999; Schneider and Rubio, 1999; Rubio and Tessele, 1997), as shown in Table 4. Higher values are only encountered in adsorption systems involving synthetic exchange ionic resins. Pillared clay was also shown to adsorb Pb, Zn, Ni, Cd, Fe and Ag efficiently (results not reported here).

The results of the three-step sequential adsorption/desorption with HCl (2% by v/v) into a Cu-pillared system are shown in Table 5. The data show that at the end of the first adsorption/desorption cycle, the K_{SD} value, for the Cu ions released, is very high (not calculated numerically), indicating strong binding of the Cu ions.

Table 4. Selected values of Cu uptake capacities of several adsorbents.

Adsorbent	Capacity (mg of Cu g^{-1})*	Authors
Solvent resins impregnated with DEHPA	4.4	Appleton <i>et al.</i> (1999)
Resin impregnated with LIX 64N	5.7	Appleton <i>et al.</i> (1999)
Derived silica gels	32.4	Appleton <i>et al.</i> (1999)
Chelating resin X - 4196	47.6	Appleton <i>et al.</i> (1999)
Ca-montmorillonite with DEHPA	56.5	Appleton <i>et al.</i> (1999)
Coal beneficiation tailing material	42.2	Féris (2001)
Zeolites	40.0	Rubio and Tessele (1997)
Non-living biomass of freshwater macrophytes <i>Potamogeton lucens</i>	41.0	Schneider and Rubio (1999)
Ca-montmorillonite with ethylenediamine	53.8	De León <i>et al.</i> (2001)
Pillared clay	110	This work
Synthetic cation exchange resin	100–317.5	Rohm and Haas (1989)

* Data taken from Langmuir sorption models

Table 5. Total amount (mg g^{-1}) of Cu adsorbed (M_{ads}) and released (M_{des}) at the end of adsorption/desorption cycles.

Cycle	Adsorption		Desorption		K_{SD}
	%	M_{ads}	%	M_{des}	
1	100	6.3	0	0	n.c.
2	97.2	12.4	17.7	2.2	5.7
3	98.8	16.4	34.2	5.6	2.9

n.c. = not calculated

After three adsorption/desorption cycles, the K_{SD} values for pillared clay show a slight decrease. This suggests that Cu ions released from the adsorbent are those adsorbed by ionic exchange processes (easy to remove by acid leaching).

The metallic complexes formed with the adsorbed organic compound presented more stability and remained within the adsorbent's structure. Presumably the highly cohesive and strongly cooperative interaction between the clay surface and the OP adsorbed enhanced the strength of metal binding, resulting in the apparent irreversibility of the adsorption process. These results are in agreement with Berkheiser and Mortland (1977) who found no $\text{Cu}(\text{phen})_3^{2+}$ was exchanged by Mg^{2+} at any concentration.

CONCLUSIONS

A Brazilian bentonite pillared by chemical adsorption of molecular 1.10-phenanthroline possesses an excellent capacity for adsorbing Cu. The quantity of OP adsorbed was 112 mg g^{-1} at pH 8.5 and showed high irreversibility (no desorption) in acidic or basic leaching solutions. Pillared clay showed a maximum uptake of Cu ions at $\sim 110 \text{ mg}$ of Cu g^{-1} of adsorbent, which represented more than 10 times the uptake capacity of the untreated bentonite. This Cu ion adsorption was independent of medium pH and is very high when compared with other known adsorbents. The amount of Cu released (desorbed) from the pillared clay was negligible in either acidic or basic solutions revealing strong binding. Mechanisms involved in the adsorption, which explain the high Cu ion uptake and irreversibility, were the metal complexation by the adsorbed OP and ionic exchange on fixed-charge (remaining) sites onto the basal plane and on the layer silicate edges. It is believed that due to these properties, pillared clay, shows much potential as an adsorbent for the removal of metal ions from effluents.

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