# Cadmium and copper adsorption on bentonite: effects of pH and particle size[1]

## Adsorção de cádmio e cobre em bentonita: efeito do pH e da granulometria

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**Abstract -** Reactions of heavy metals with clay minerals are important in determining metal fates in the environment. However, the adsorption process of these metals by the bentonite has been extensively investigated. The objectives of this work were to assess the ability of bentonite clay to adsorb cadmium and copper and to study the effects of pH and particle size upon these metals adsorption. Adsorption isotherms were obtained from batch adsorption experiments, with increasing cadmium and copper concentrations (5-200 mg L$^{-1}$). To find out the effects of pH and particle size on adsorption, the experiments were conducted at pH 4; 5 and 6 using particles sizes of < 0.5 mm and 0.5 to 2.0 mm . The difference between initial and final cadmium and copper concentrations was assumed to be the amount adsorbed by bentonite. The bentonite adsorbed more copper than cadmium, both metals adsorption increased with increasing pH for both particle sizes. No effect of particle size was observed. Experimental data were best fitted to Langmuir model.

**Key words -** Clay mineral. Heavy metals. Isotherms. Langmuir.

**Resumo -** As reações dos metais pesados com os minerais de argila são importantes para determinar o destino dos mesmos no meio ambiente. Assim, o processo de adsorção destes metais pela bentonita tem sido muito investigado. Objetivou-se com este trabalho avaliar a capacidade da argila bentonita em adsorver cádmio e cobre e os efeitos do pH e de sua granulometria na adsorção dos mesmos. A partir de experimentos tipo "batch", foram elaboradas isotermas de adsorção com quantidades crescentes de Cd e Cu (5-200 mg L$^{-1}$). Para determinar o efeito do pH e da granulometria sobre a adsorção, os experimentos foram conduzidos a pH 4; 5 e 6, utilizando bentonita com granulometria < 0,5 mm e entre 0,5 a 2,0 mm. As quantidades de Cd e Cu adsorvidas pela bentonita foram determinadas pela diferença entre as concentrações inicial e final dos elementos na solução de equilíbrio. A bentonita adsorveu mais Cu do que Cd, entretanto a adsorção dos dois metais aumentaram com o aumento do pH independentemente da granulometria. Nenhum efeito da granulometria sobre a adsorção foi observada. Os dados experimentais foram bem ajustados ao modelo de Langmuir. A capacidade máxima de adsorção diminuiu e a energia de ligação aumentou em função do aumento do pH.

**Palavras-chave -** Mineral de argila. Metais pesados. Isotermas. Langmuir.

## Introduction

Pollution by heavy metals is a serious environmental problem facing life of earth. Heavy metals are stable and persistent environmental contaminants since they cannot be degraded or destroyed (LACIN et al., 2005). They may be present in soils from a variety of sources and can represent a potential hazard to humans and the environment if they are readily released into soil solution or are other-wise available to biological processes. However, if such metals are bound up in relatively inert and insoluble compounds, the danger they represent is reduced substantially (SNEDDON et al., 2006).

Cadmium and copper are naturally occurring, potentially toxics and mobile and litter mobile elements, respectively, present in most soil environments. Increasing amounts of them are added to soil through city wastes, sewage sludge, pesticides and fertilizer applications. The persistence and mobility of those elements in soils is determined largely by the extent of adsorption by soil particles.

Owing to their adsorption capacity, aluminosilicate and oxide minerals are capable of removing many metals from soil, aqueous solutions and waste waters (ÁLVAREZ-AYUSO; GARCIA-SÁNCHEZ, 2003) over a wide pH range. Then, clay minerals like bentonite, vermiculite and illite (BEREKET et al., 1997; LACIN et al., 2005; MELLAH; CHEGROUCHE, 1997; RODRIGUES et al., 2004; SANTOS et al., 2002; SILVA et al., 2009) and Fe oxide minerals such as goethite (MUSTAFA et al., 2004), have been extensively used for metal removal. The process involves precipitation, ion exchange and adsorption.

One such natural clay is bentonite, which is primarily a Na-montmorillonite, whith a 2:1 layered silicate (LACIN et al., 2005). The substitution of $Al^{3+}$ and $Mg^{2+}$ for $Si^{4+}$ and $Al^{3+}$, in the tetrahedral and octahedral layer, respectively, results in a net negative surface charge on the clay which is important for the adsorption process which depends on pH and surface particle.

Lancin et al. (2005) found that the bentonite samples used for are appropriate for adsorption of Cd (II) cations, removing 96.84% from aqueous solutions, and that the pH has positive effects on Cd (II) adsorption. In the study presented by Dal Bosco et al. (2006), the montmorillonite

samples removed 98.3% of Cd (II) from aqueous solutions and Cd adsorption increasing with the pH. According to Alvarez-Ayuso and Garcia-Sánchez (2003) Na-bentonite presented maximum sorption capacities of 26.2 mg g$^{-1}$ Cd and 30.0 mg g$^{-1}$ Cu.

The purpose of this work was to assess the ability of bentonite clay to adsorb cadmium and copper from aqueous solutions and to investigate the influence of pH and particle size upon these metals adsorption by bentonite clay. The experimental results were analyzed by fitting Langmuir isotherms. Adsorption isotherms describe the relationship between the mass of the adsorbed substance (adsorvate) by the solid (adsorvent) and the concentration of the substance in the solution in equilibrium. Despite their limitations, Langmuir model has been used in various studies of adsorption (ALLEONI, 2003; ALLEONI et al., 2005; ÁRIAS et al., 2005; CASAGRANDE et al., 2004; CHAVES et al., 2009; GARCIA-SÁNCHEZ et al., 1999; SILVEIRA; PIERANGELI et al., 2009) and through it is possible to express mathematically some of the soil or clay properties, such as the nature of the adsorption processes (JORDÃO et al., 2000). Furthermore, the maximum adsorption parameter may be used as an indicator to compare adsorbent surface with different characteristics, as well as the effects of several other factors.

## Material and methods

The natural bentonite used as an adsorbent in this study was obtained from the city of Boa Vista, State of Paraiba, Brazil. The bentonite samples were air dried at room temperature, crushed, grounded and sieved through a 0.5 and 2.0 mm screen. Chemical analyses were performed according to Embrapa (1997) (TAB. 1).

X ray diffraction (XRD) was used to characterize the dried samples. XRD analysis was performed on a XRD 6000 Instrument using CuKα (40kV/30mÅ) radiation. The goniometer calibration was checked daily and the scan performed covered 5 to 75º 2θ using unfiltered Cu radiation, with interpolated step sizes of 0.02º, and 1.2min/step counting time. Figure 1 represents XRD of bentonite showing characteristic peaks of the smectite clay, the main component of bentonite, as wel as the presence, in smaller amounts, peaks of silicon oxide.

**Table 1** - Chemical composition of the natural bentonite

| pH H$_2$O (1:2.5) | Ca$^{2+}$ | Mg$^{2+}$ | Na$^+$ | K$^+$ | H$^+$ | Al$^{3+}$ | CEC | P | O.M. |
|---|---|---|---|---|---|---|---|---|---|
| | --------------------------------------------cmol$_c$ kg$^{-1}$-------------------------------------- | | | | | | | mg dm$^{-3}$ | g kg$^{-1}$ |
| 7.0 | 20.74 | 35.97 | 7.06 | 0.24 | 0.0 | 0.0 | 64.01 | 2.9 | 26 |

**1** - Smectite

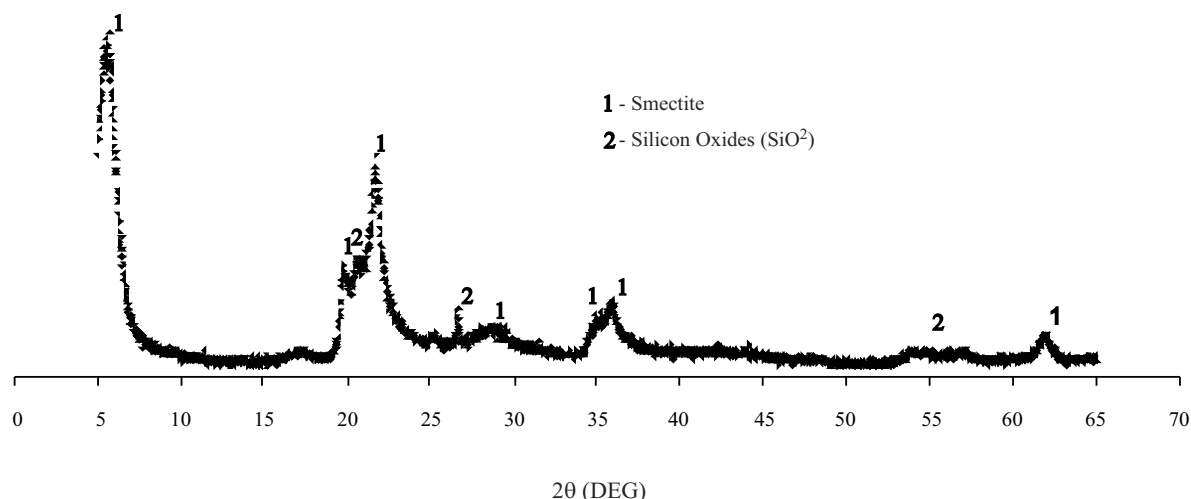**2** - Silicon Oxides ($SiO_2$)

**Figure 1** - X-ray diffraction patterns of the Bentonite. Asterisks denote the peak positions for a smectite (1) and silicon oxides (2)

The adsorption of Cd and Cu was studied in batch equilibrations involving duplicate 2 g of bentonite samples in 50 mL capacity polyethylene tubes with 20 mL of Cd and Cu solutions containing 5; 10; 20; 30; 50; 100; 120 and 200 mg Cd or Cu $L^{-1}$. To evaluate the effect of equilibrium pH on the adsorption of the cations by the bentonite, the pH of bentonite-solution system was adjusted to pH 4.0; 5.0 and 6.0, separately, by adding dilute solution of either HCl 0,1 N or NaOH 0,1 N (GARCIA-SÁNCHEZ et al., 1999). After this adjustment, the tubes were shaken for 2 h and left still for 24 h. At the end of equilibration, the supernatant was filtered through a filter paper and Cd and Cu concentration of the filtrate determined by an atomic absorption spectrophotometer. The difference between initial (Ci) and final (Cf) Cd and Cu concentrations was considered as the amount of Cd and Cu adsorbed by bentonite. The percentage (%) adsorption yields was calculated as: % ads = [(Ci - Cf)/ Ci] x 100.

During the first and second series of adsorption experiments was used bentonite samples sieved through a 0.5 and 2.0 mm screen, respectively.

The experimental adsorption data was fitted with Langmuir adsorption isotherm: X = (KbC)/(1+KC) where X is the amount of Cd or Cu retained by unit weight of bentonite solids, mg $g^{-1}$; K the Langmuir adsorption coefficient, b the maximum amount that can be adsorbed and C the concentration of Cd or Cu in equilibrium solution, mg $L^{-1}$.

## Results and discussion

In general, the percentage of sorção for both metals increased as the pH increased, and at any pH it decreased with the initial metals concentration (TAB. 2). In this case with the increase in the metal concentration, more substitution sites of the clay were filled and Cd and Cu retention became more difficult. Increasing pH has implications upon the magnitude of electric charges, i.e., increases the negative charges in surface clay and consequently increases cationic heavy metal adsorption. On the other hand, the particle size seems to have little influence on the percentage of metals adsorption.

The adsorption isotherms are important in determining the adsorption capacity of cadmium (Cd) and copper (Cu) by the natural bentonite. The experimental data were fitted to Langmuir linear equation with correlation coefficients varying between 0.80 and 0.99 for Cu and between 0.97 and 0.99 for Cd, indicating that Langmuir model (Hyperbolic Langmuir adsorption isotherms) adjust well to diverse metal concentration (FIG. 2) which has been used in several studies of adsorption (ALVAREZ-AYUSO; GARCIA-SÁNCHEZ, 2003; ÁRIAS et al., 2005; BEREKET et al., 1997; GARCIA-SÁNCHEZ et al., 1999; MELLAH; CHEGROUCHE, 1997). Similar results were obtained by Bereket et al. (1997) and Dias et al. (2001), working with clay and soil, respectively, using Langmuir model.

The inclination of the Cu adsorption curves, mainly at pH 5 and 6, showed that the increase in Cu adsorption was higher at the lowest concentration of the metal. As the concentrations increased, the adsorption rate was less pronounced. In bentonite Cu seems to reach saturation which means that the metal had filled possible available sites and further adsorption could take place only at new surfaces (BEREKET et al., 1997).

Regardless particle size, Cd and Cu adsorption increased with increasing pH. This behavior agrees with

**Table 2 -** Adsorption yields of cadmium and copper at pH 4, 5 and 6 for different particle size of bentonite

| Initial metal concentration | Cadmium adsorption (%) | | | | | | Copper adsorption (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| mg L⁻¹ | Particle size < 0.5 mm | | | Particle size 0.5 - 2.0 mm | | | Particle size < 0.5 mm | | | Particle size 0.5 - 2.0 mm | | |
| | pH 4 | pH5 | pH 6 | pH 4 | pH5 | pH 6 | pH 4 | pH5 | pH 6 | pH 4 | pH5 | pH 6 |
| 5 | 85.33 | 90.67 | 94.67 | 86.00 | 90.67 | 95.33 | 99.04 | 97.53 | 99.04 | 99.04 | 99.38 | 98.31 |
| 10 | 85.53 | 90.57 | 94.34 | 86.79 | 91.19 | 94.34 | 95.57 | 98.14 | 99.23 | 96.84 | 99.32 | 98.76 |
| 20 | 84.83 | 90.21 | 93.84 | 86.41 | 90.68 | 94.31 | 91.80 | 97.98 | 98.27 | 91.54 | 97.41 | 98.25 |
| 30 | 84.44 | 90.07 | 93.16 | 84.99 | 90.07 | 93.16 | 89.55 | 97.17 | 97.67 | 90.17 | 97.01 | 97.59 |
| 50 | 83.46 | 89.00 | 92.38 | 84.31 | 89.71 | 92.51 | 89.47 | 96.86 | 97.01 | 89.52 | 97.93 | 97.17 |
| 100 | 82.06 | 86.77 | 89.35 | 83.00 | 87.24 | 89.95 | 88.84 | 94.22 | 94.37 | 89.58 | 94.90 | 94.71 |
| 120 | 80.38 | 84.54 | 87.40 | 80.22 | 85.40 | 87.63 | 88.84 | 91.90 | 92.53 | 86.61 | 92.16 | 92.33 |
| 200 | 78.71 | 82.02 | 85.61 | 78.78 | 82.63 | 85.51 | 79.04 | 88.36 | 90.35 | 81.77 | 87.34 | 90.59 |
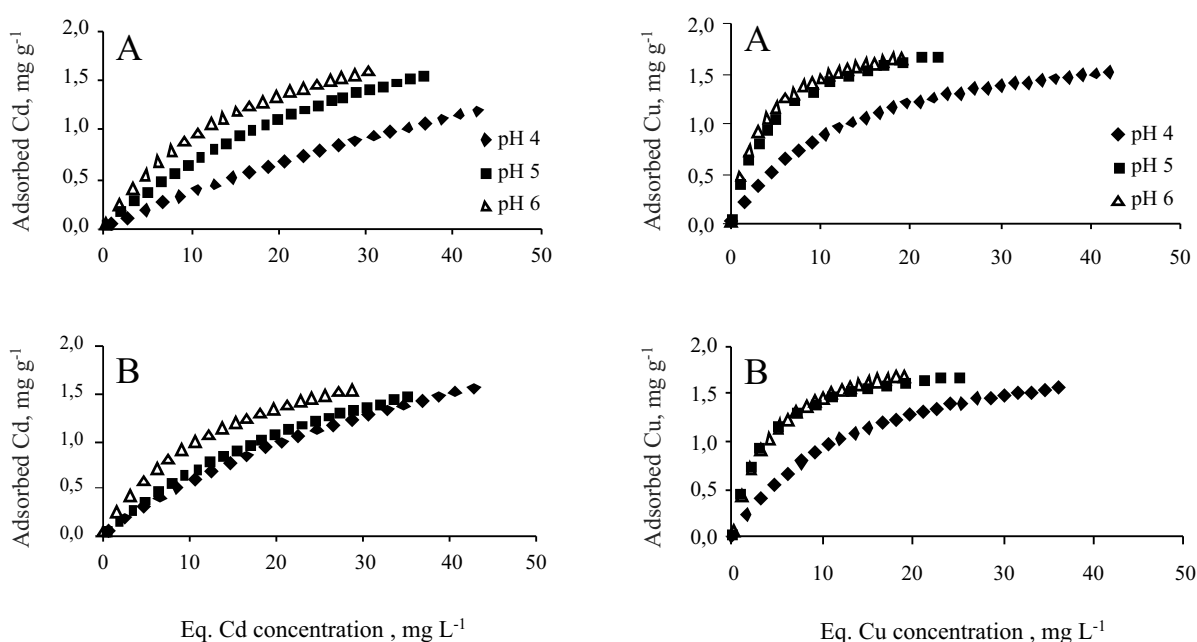


**Figure 2 -** Langmuir adsorption isotherms of cadmium and cooper on bentonite at pH 4; 5 and 6 for different particle sizes (A = < 0.5 mm; B = 0.5 - 2.0 mm)

the results presented in Table 2 and with the results previously found on the adsorption of heavy metals by the soil (ALLEONI et al., 2005; APPEL; MA, 2002; NAIDU et al., 1997; SOARES et al., 2009) or pure clay (CHUI, 2005; CORNU et al., 2003; LACIN et al., 2005; SANTOS et al., 2002). The results support the observation that increasing bentonite-solution system pH led, initially, to an increase in net negative surface charge on bentonite where Cd and Cu are adsorbed by a single binding mechanism (NAIDU et al., 1997). This can be due to the deprotonation of the most active surfaces of bentonite as a result of surface hydrolysis with increase in pH from 4 to 6.

However it is interesting to notice that Cu adsorption was similar in both 5 and 6 pH´s and that there was difference only between pH 4 and 6 (the means 90.27 b and 96.06 a, respectively, followed by the different letter differed by Tukey test at 0.05 level, to particle size < 0.5 mm). At low pH values has high $H^+$ concentration in the solution, which increases the competition for exchange sites on clay hindering the adsorption of heavy metals (DAL BOSCO et al., 2006). On the other hand, according to Alleoni et al. (2005), with increasing pH, the ions $CuOH^+$ concentration increases rapidly and they are adsorbed in larger amounts than ion $Cu^{++}$. Probably the $CuOH^+$ concentration was

more pronounced when the pH increased from 4 to 5 and less pronounced with increasing pH from 5 to 6, which contributed to the adsorption behavior of metal in these pH values were similar. However, to raise the pH from 5 to 6 was used a larger amount of NaOH, which may have reacted with $Cu^{++}$, leading to precipitation of hydroxides species coordinated such as $Cu\,(OH)^+$ (SANTOS et al., 2002) preventing the copper being adsorbed.

The increase in Cd adsorption was also attributable to the hydrolysis reaction and to the increase in Cd hydroxil species in solution. Because the $CdOH^+$ ion is monovalent, the energetic barrier that must be overcome when it comes closer to the surface of the particle is smaller than in the case of the $Cd^{2+}$ ion (CASAGRANDE et al., 2004). In spite of the fact that at low pH the amount of $CdOH^+$ corresponds to a small proportion of the Cd species in solution the adsorbed amount increases with pH because the hydrolysis reaction is continuously processed and the colloid surface may have an accelerating effect

on that reaction. Furthermore, as pH increases, hydrogen ions are released, which favor Cd adsorption at the colloid surface (SOARES et al., 2009).

According to Mellah and Chegrouche (1997), working with bentonite, the zinc adsorption rate was slightly improved when the particle size decreased. This is due to the fact that the surface area increases with decreasing particle size. However this was not observed in this work. This can be explained in terms of the methodology used. Probably, when the bentonite-solution system was shaken, the largest particles broke up resulting in smaller ones, with specific surface similar to those particles < 0.5 mm.

Figure 3 shows that, with exception of the adsorption of Cd at pH 4, the adsorption of this element at pH 5 and 6 and the adsorption of Cu at all pH values, practically, were not influenced by the particle size of bentonite, which is demonstrated by the overlap of the curves in the graphs.
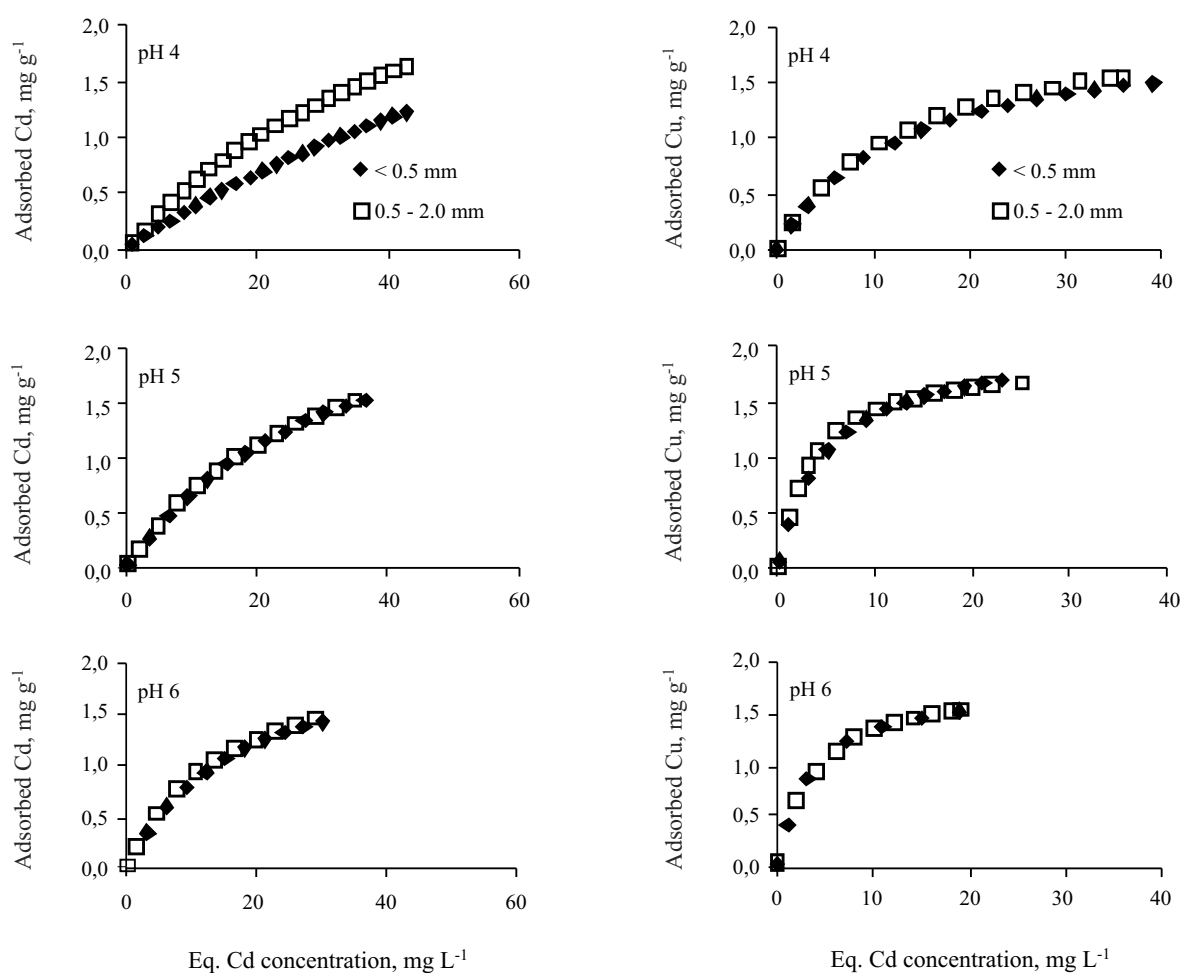


**Figure 3 -** Langmuir adsorption isotherms of cadmium and cooper on bentonite at different size particle at fixed pH

**Table 3 -** Langmuir parameters of adsorption of cadmium and copper on bentonite as a function of pH and particle size

| Metal | Particle size Mm | K ----------------(L mg$^{-1}$)---------------- | | | b ----------------(mg g$^{-1}$)---------------- | | |
|---|---|---|---|---|---|---|---|
| | | pH 4 | pH5 | pH 6 | pH 4 | pH5 | pH 6 |
| Cadmium | < 0.5 | 0.01 | 0.03 | 0.06 | 4.09 | 2.94 | 2.47 |
| | 0.5 - 2.0 | 0.02 | 0.03 | 0.07 | 3.54 | 3.00 | 2.42 |
| Copper | < 0.5 | 0.08 | 0.21 | 0.30 | 1.97 | 2.04 | 1.95 |
| | 0.5 - 2.0 | 0.08 | 0.31 | 0.26 | 2.11 | 1.88 | 2.02 |

From the linear adsorption isotherms, the Langmuir constants for Cd and Cu were calculated (TAB. 3). Although the pH increase in the bentonite-solution system produced an increase in the Cd and Cu adsorption, the shape of adsorption isotherms showed, in some situations, that adsorption maximum (b) can occur at lower pH (TAB. 3).

When pH increased from 4 to 6 the values of maximum Cd and Cu adsorption (b) decreased, being this behavior more pronounced for the Cd; the Cu situation was similar. On the other hand the bonding energy (K) increased with the pH. This indicates that at higher pH values Cd and Cu are adsorbed more strongly as it is evident from the data showed in Table 3. Stronger binding of Cd and Cu onto bentonite may be due to increase in Cd and Cu hydroxyl species in solution.

## Conclusions

1. Bentonite clay from Boa Vista, Paraíba State, Brazil, can be used as adsorbent for the removal of Cd and Cu from aqueous systems, being the clay more efficient for the copper adsorption. It was also found that adsorption of both metals increased with the pH in both particle size;

2. In general, particle size had not effect on Cd and Cu adsorption;

3. The maximum capacity of adsorption decreased and the bonding energy increased with increasing pH. At the lowest pH there is the possibility of Cd and Cu ions previously adsorbed onto bentonite be released to environment. The release of Cd should be easier than the Cu since it presented less bonding energy.

## Acknowledgment

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