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# Evaluation of $Cu^{2+}$ Ions Adsorption Equilibrium in Calcined Bentonite Clay and after Treatment with Sodium

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Industrial activities are responsible for the increasing environmental degradation through unsustainable consumption of natural resources and the improper disposal of various wastes. In Brazil, of all generated wastes, effluents containing heavy metals are causing more problems, because they have negative effects on the ecosystem, leading to reduced water quality which harms aquatic life, wildlife, flora, and also human health. Hence, effluents containing heavy metals have to suffer a purification treatment to remove these microcontaminants. There are several processes used to remove metal ions from wastewater, among which adsorption presents greater possibilities of use, because it is very effective in removing heavy metals even in low concentrations. Therefore, this work aims to evaluate the $Cu^{2+}$ ion adsorption equilibrium in calcined bentonite clay and clay after calcination and sodification (dispersed sodium clay) treatments. Adsorption isotherms were obtained at environmental temperature (25 °C). Langmuir, Freundlich and Dubinin-Radushkevich models were applied to fit the experimental data. It was observed an influence on the sodification treatment of the clay in its $Cu^{2+}$ ion removal capacity, depending on the ion exchange mechanism involved.

## 1. Introduction

The contamination of water bodies by toxic metal originated from industry activity, domestic sewage, and urban storm runoffs is of great concern due the harm to human health and environment (Kaewsarn, 2002). When present, even in low concentrations, it depicts non-biodegradability, elevated persistence characteristics and its capability of bioaccumulation (Oorts, 2012). Copper is a crucial metal, with important roles in several enzymes, however, in excess may cause damage, due accumulation, to the liver, pancreas and brain (El-Bayaa et al., 2009). The ample usage of this toxic metal, from industries to agricultural practices, has resulted in significant anthropogenic emission causing a wide contamination of soils and surface waters (Oorts, 2012). Thus, it is necessary the implementation of more rigorous environmental laws, preventing this contaminant entrance in the environment (Flouty and Estephane, 2012).

The removal of metals from effluents may be achieved from chemical precipitation, ion exchange, membrane separation, adsorption, and others. Factors such as costs and metal encumbered sludge are downsides of some of these treatments (Weng et al., 2007). The adsorption process has become one of the preferred methods for removal of toxic contaminants from effluents since it is effective, even when contaminants are present in low concentration, economical, when the most suitable adsorbent material is selected, and results in minimal sludge production (Mohanty et al., 2006). The most commonly used adsorbent is activated carbon, a material with elevated adsorption capacities but with disadvantages regarding costs, due preparation, as well as, regeneration due difficulties in the separation from the effluent when powdered activated carbon is used (Weng et al., 2007). Hence, there is a continuing search for low-cost, efficient alternative materials such as sericin particles (Andrade et al., 2016), alginate residue (Cardoso, et al., 2016), garden grass (Hossain et al., 2012), and marine algae biomass (Kaewsarn, 2002).

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Clays are potential adsorbent materials due its high surface area, mechanical stability, and various structural and surface properties resulting in a material with high adsorption capacity (Bekçi et al., 2006). Clays have been employed in the removal of copper and silver (Freitas et al., 2017), copper and chromium (El-Bayaa et al., 2009), and copper (Gimenes et al., 2013). Consequently, this work aims to compare the $Cu^{2+}$ ions adsorption equilibrium by calcined bentonite and clay after calcination and sodification treatments.

## 2. Materials and Methods

### 2.1 Adsorbent

The clay material the bentonite variety Bofe, originally from the Northeastern region of Brazil (Boa Vista-PB), was donated by Dolomil LTD and used as an adsorbent material. The clay material was sieved in Tyler sifter to achieve the medium particle size of 0.855 mm. Following this step, the clay was calcined at 500 °C for 24 hours in order to increase the mechanical resistance, promote dihydroxylation, and eliminate impurities; this way enhancing the material's adsorption capacity. In order to compare the adsorption capacities with the calcined Bofe, the raw clay underwent a Sodium ions treatment (dispersed sodium clay). The material was put in contact with a 1 % NaCl (pH 3) solution at room temperature and constant stirring for 3 hours. The clay was then filtrated, dried at 60 °C for 48 hours, sieved for size classification, and calcined at 500 °C for 24 hours.

### 2.2 Metal solution

Copper solutions varying from 0 to 10 mmol/L were prepared by dissolving $Cu(NO_3)_2.3H_2O$ (Vetec) in 100 mL of DI water. The pH was adjusted according the metal speciation in order to avoid the metal's precipitation and to ensure the adsorption process. By metal speciation study it was possible to identify the different metal compounds according to different pH values. Therefore, nitric acid and ammonium hydroxide were used to adjust pH of the metal solution. A pH meter (Gehaka 1800) was used to measure the pH of the solutions.

### 2.3 Metal Speciation

In the present work, the Chemical Equilibrium Diagrams were obtained by simulation with the Hydra/Medusa Software (Puigdomenech, 2004). The study of metal speciation is necessary in order to identify different metals compounds present in solution as a function of pH, the result showed that the ideal pH range was below 4.5 and therefore the range 3.5 – 4.5 was implemented, ensuring the adsorption process and avoiding the metal's precipitation.

### 2.4 Equilibrium assays

In order to obtain adsorption isotherms, 0.5 g of adsorbent was added to 50 mL of each copper solution described in Section 2.2 at 25 ºC and constant stirring of 200 rpm, in a shaker (Jaio Tech). After the equilibrium was reached (6 h), solid and liquid phases were separated at 4000 rpm for 10 min. The initial and final metal concentrations were measured by atomic absorption (AA-7000 Shimadzu).

### 2.5 Equilibrium models

Adsorption equilibrium may be well represented by equilibrium isotherms, which is obtained by plotting equilibrium adsorbed amount ($q_e$) vs. equilibrium concentration ($C_e$). In order to evaluate adsorption process, equilibrium models may be adjusted to experimental data, based on empirical or theoretical assumptions.
Langmuir model, which is a theoretical model, may be well represented by Eq(1).

$$q_e = \frac{q_{max}.K_L.C_e}{1 + K_L.C_e} \qquad (1)$$

where $q_e$ is the equilibrium adsorbed amount (mmol/g), $q_{max}$ is the maximum adsorbed amount (mmol/g), $K_L$ is a constant related to adsorbent affinity for metal ions (L/g), and $C_e$ is the equilibrium concentration (mmol/L). Langmuir (1918) developed this model considering a finite number of active sites, monolayer adsorption and uniform process (Ruthven, 1984).
From Langmuir model, it is also possible to calculate the constant $R_L$, as shown in Eq(2).

$$R_L = \frac{1}{1 + K_L.C_0} \qquad (2)$$

where $C_0$ is the highest metal concentration used (mmol/L). From that, it is possible to evaluate equilibrium behaviour. In case of $R_L > 1$, the equilibrium is not favourable; for $R_L = 1$, it is considered a linear equilibrium; when $R_L = 0$, the equilibrium is irreversible; and in case of $0 < R_L < 1$, the equilibrium is favourable.
Another equilibrium model is the empirical Freundlich model. It considers heterogeneous surface and does not predict adsorbent saturation due an infinite number of active sites (Akar et al., 2009). This model is well represented by Eq(3).

$$q_e = K_F . C_e^{1/n} \tag{3}$$

where $K_F$ is a constant indicating the adsorption extension (L/mmol) and n is an empirical dimensionless constant.

Dubinin-Radushkevich (D-R) model is a more general model, since it does not consider homogeneous surface or constant sorption potential. It may be represented by Eq(4) (Kilislioglu and Bilgin, 2003).

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{4}$$

where $q_m$ is the theoretical adsorption capacity (mmol/g) and ε is the Polanyi potential, obtained by Eq(5).

$$\varepsilon = R\, T \ln\left(1 + \frac{1}{C_e}\right) \tag{5}$$

From D-R model, it is possible to analyze the adsorption energy by Eq(6).

$$E = \frac{1}{\sqrt{2\beta}} \tag{6}$$

In case of $E < 8.0$ kJ/mol, it is said to be a physical adsorption process, and in case of $8.0 < E < 16.0$ kJ/mol, it is considered an ion-exchange reaction.

### 2.6 Morphological examination (SEM)

In order to analyse the surface morphology of the adsorbent material a scanning electron microscopy (SEM) analysis was performed. The samples were metalized with a thin layer of gold. The photomicrographs were taken at an acceleration voltage of 10 kV in electron microscope (440i, Electron Microscope LEO, England). Also chemical composition was determined through Energy Dispersive X-ray Microscopy (EDX) using a detector (7060, Oxford).

## 3. Results and Discussion

### 3.1 Equilibrium assays

Adsorption equilibrium data for copper using calcined bentonite clay and sodic treated clay are reported in Figure 1.

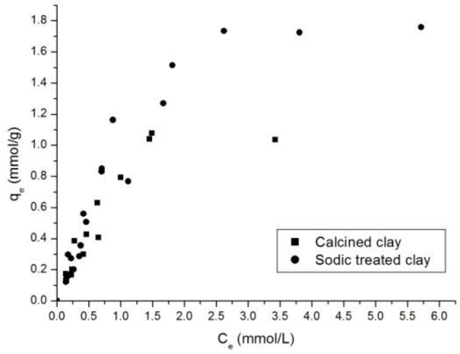
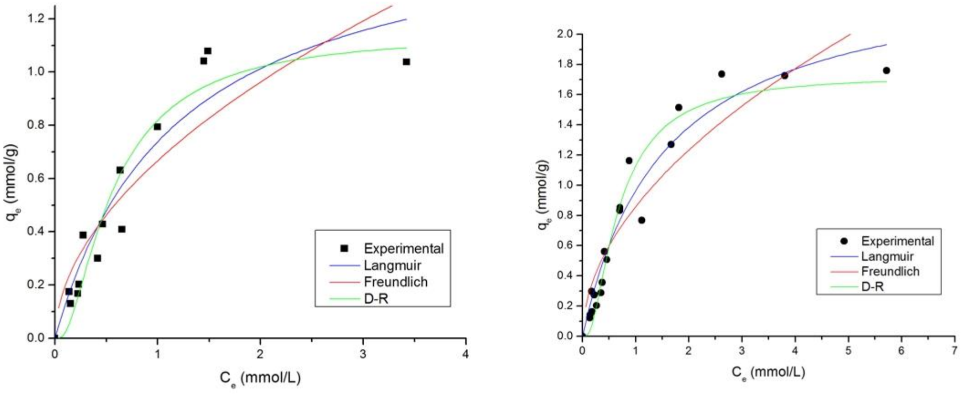


*Figure 1: Copper adsorption isotherms for calcined and sodic treated clay.*

From Figure *1* it can be observed that sodic treated clay provided a higher adsorbed amount than calcined clay. Probably due ionic exchange improvement obtained with the sodic treatment, which was also observed by Almeida Neto et al. (2014). In that case calcined clay and sodic treated clay were compared in copper adsorption in fixed bed system. The treatment with sodium improved the clay adsorption capacity, as well as it was observed in this work, in batch system. Both isotherms from Figure *1* presented similar behaviors indicating extremely favorable equilibrium, a fact characterized by the shape of the curves. Langmuir, Freundlich, and Dubinin-Radushkevich equilibrium models were adjusted to experimental data with the Origin® software, as shown in Figure 2. The obtained parameters and regression coefficients are depicted in Table 1.



(a) (b)

*Figure 2: Copper adsorption isotherms adjusted to Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) models: (a) calcined clay; (b) sodic treated clay.*

*Table 1: Obtained parameters by equilibrium models adjustment.*

| Model | Parameter | Calcined clay | Sodic treated clay |
|---|---|---|---|
| Experimental | $q_e$ (mmol/g) | 1.052 | 1.740 |
| Langmuir | $q_{max}$ (mmol/g) | 1.612 | 2.453 |
| | $K_L$ (L/mmol) | 1.183 | 1.543 |
| | $R_L$ | 0.159 | 0.080 |
| | $R^2$ | 0.914 | 0.948 |
| Freundlich | $K_F$ (L/mmol) | 0.667 | 0.858 |
| | n | 1.893 | 1.912 |
| | $R^2$ | 0.815 | 0.872 |
| Dubinin-Radushkevich | $q_m$ (mmol/g) | 1.142 | 1.726 |
| | β (mol².kJ²) | 0.014 | 0.002 |
| | E (kJ/mol) | 5.976 | 15.81 |
| | $R^2$ | 0.924 | 0.944 |

According to the regression coefficients, the best adjustment was obtained for Langmuir and Dubining-Radushkevich models, indicating that Freundlich assumption of infinite active sites is not suitable in this case. Langmuir model provided maximum adsorbed amount for both adsorbents as 1.612 mmol/g for calcined clay and 2.453 mmol/g for sodic treated clay, showing that sodic treated clay presents higher adsorption capacity for copper ions, when compared to calcined clay. This is a good result when compared to other adsorbents in literature. Fouladgar et al. (2015) obtained $q_{max}$ 0.493 mmol/g in copper adsorption on alumina nanoparticles and Ben-Ali et al. (2017) evaluated copper adsorption on raw pomegranate peel and obtained $q_{max}$ as 0.474 mmol/g. Thus, the clay evaluated in the present work is a promising adsorbent for copper removal. Langmuir model also provided parameters $R_L$, which remained between 0 and 1.0 indicating a favorable equilibrium.

From D-R model, adsorption capacity represented by $q_{max}$ is also higher for sodic treated clay. Adsorption energy (E) indicates that calcined clay suffers a physical adsorption ($E < 8$ kJ/mol) as well as in case of sodic treated clay it occurs a chemical adsorption process ($8 < E < 16$ kJ/mol), which is equivalent to ion-exchange. This confirms the ionic exchange improvement obtained after clay sodic treatment.

The adsorption comparison of the two clays was done, using an independent statistical analysis. The mean capacities of the two clays were compared performing a two sample t-test, after a logarithmic transformation of the equilibrium adsorption amount. This logarithmic transformation reduced the dispersion and the asymmetry in the data distribution. The results suggested that the difference in adsorption capacity is significant with a p-value of 0.039 (t-value of -2.14), considering a significance level of 0.05. This is an evidence that sodic treatment improved the adsorption capacity.

### 3.2 Morphological examination (SEM)

Calcined clay and sodic treated clay were analysed by Scanning Electron Microscopy (SEM) and the micrographs obtained for clays before and after adsorption process with magnification of 2000x are shown in Figure 3.

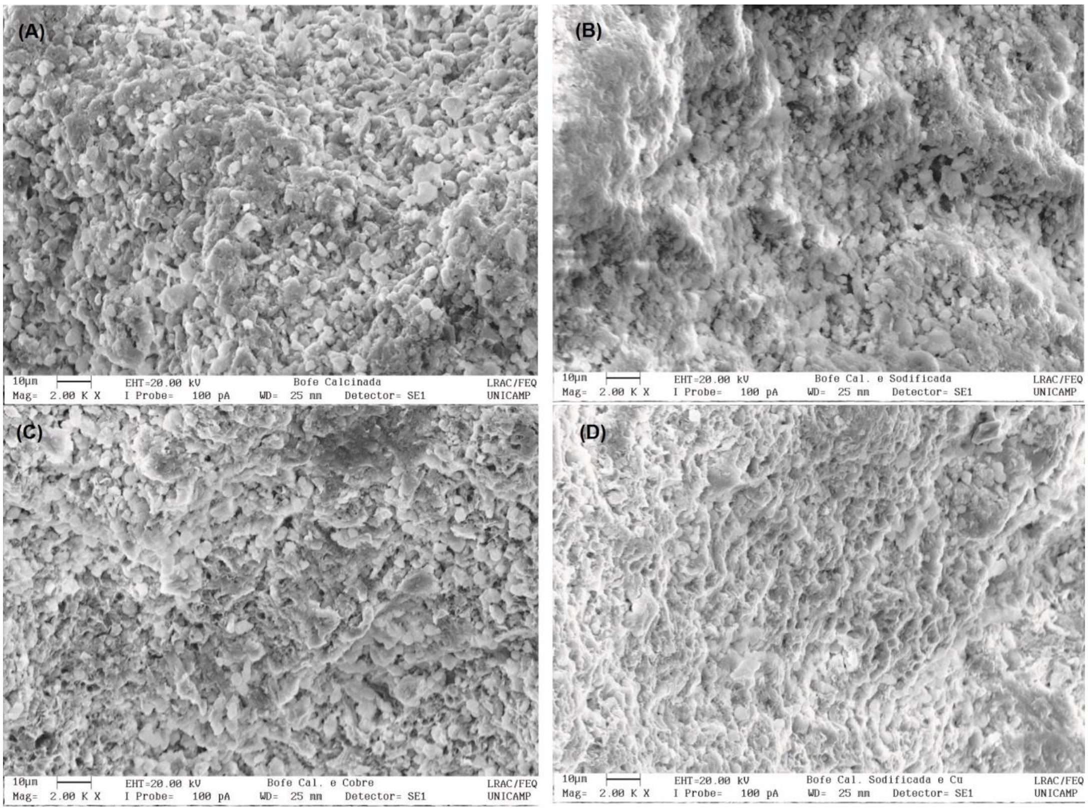


*Figure 3: SEM micrographs for (A) calcined clay; (B) sodic treated clay; (C) calcined clay after adsorption; (D) sodic treated clay after adsorption*

It can be verified from Figure 3 that no significant changes occurred in clay after adsorption process. By comparing the calcined clay and sodic treated clay, it can be observed a more homogeneous surface in clay after sodic treatment. The calcined clay presented small particles, which disappeared after the contact with sodium. Table 2 presents the element mass percentage obtained by Energy Dispersive X-ray Microscopy for the samples shown in Figure 3.

*Table 2: Element mass percentage composition for calcined clay and sodic treated clay after adsorption process.*

| Element | C | O | Na | Mg | Al | Si | K | Ca | Ti | Fe | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Calcined clay | 11.37 | 53.51 | 0.39 | 0.92 | 5.14 | 25.24 | 0.29 | 0.50 | 0.17 | 3.03 | - |
| Sodic treated clay | 19.86 | 52.32 | 0.88 | 0.63 | 3.87 | 19.36 | 0.16 | 0.19 | 0.24 | 2.56 | - |
| Calcined clay + $Cu^{2+}$ | 19.97 | 55.64 | - | 0.73 | 3.89 | 17.54 | - | 0.20 | 0.17 | 1.62 | 0.25 |
| Sodic treated clay + $Cu^{2+}$ | 19.79 | 56.47 | - | 0.64 | 3.86 | 16.85 | 0.08 | 0.15 | 0.17 | 1.65 | 0.39 |

Table 2 results show that the sodium ion present in the clay prior adsorption does not remain after adsorption. In fact, they seem to be replaced by copper ions. This proves the ion-exchange occurrence during adsorption process. In addition, ions such as potassium and iron are reduced after the adsorption process, suggesting that they may have being substituted by copper ions. The same behaviour was observed for calcium in calcined clay.

## 4. Conclusions

Both calcined clay and calcined and sodic treated clay showed efficient at copper removal, with maximum adsorption capacity of 1.612 mmol/g and 2.453 mmol/g, respectively. Considering these results, sodium treatment was effective at improving clay adsorption capacity, proving the advantage of its application. Langmuir and Dubinin-Radushkevich models presented the best adjustments, showing the tendency for a monolayer and uniform adsorption. In addition, the D-R model indicated that the calcined clay was of a physical adsorption nature and the sodic treated clay presented propensity to an ion-exchange reaction. SEM analysis showed that the sodic treatment modified the clay surface, leading to a more homogeneous appearance. EDX analysis proved the ion exchange occurrence, once, ions found in clay prior adsorption did not remain in the clay after the adsorption process, being replaced by copper ions after adsorption.

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