Zinc adsorption in bentonite clay: influence of pH and initial concentration

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ABSTRACT. This paper evaluated the adsorption capacity of zinc by Bofe bentonite clay. Bofe clay was subjected to a thermal treatment for optimizing its adsorption capacity. The kinetic equilibrium of the process was studied in a finite bath system and experiments were performed by varying pH, the amount of adsorbent and initial concentration of the metal. The Langmuir and Freundlich models were used for the analysis of adsorption equilibrium. The physicochemical characterization of clay, before and after the adsorption process, included the techniques of scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction and N_2 physisorption. The calcined Bofe clay is able to remove zinc from synthetic wastewater. Langmuir model provided the best fit for sorption isotherms with a maximum amount of metal adsorbed of 4.95 mg of metal g^{-1} of calcined clay. The adsorption was strongly influenced by the initial conditions and modifies the physicochemical characteristics of the clay.
Keywords: "Bofe", heavy metal, wastewater.

Adsorção de zinco em argila bentonita: influência do pH, quantidade de adsorvente e concentração inicial

RESUMO. Este trabalho teve como objetivo avaliar a capacidade de adsorção de zinco pela argila bentonítica Bofe. A argila Bofe foi submetida a um tratamento térmico para otimização de sua capacidade de adsorção. O equilíbrio cinético do processo foi estudado em um sistema de banho finito e experimentos foram realizados variando o pH, a quantidade de adsorvente e a concentração inicial de metal. Os modelos de Langmuir e Freundlich foram utilizados para a análise do equilíbrio de adsorção. A caracterização físico-química da argila, antes e após o processo de adsorção, envolveu as técnicas de microscopia eletrônica de varredura, espectroscopia de energia dispersiva de raios-X, difração de raios-X e fisissorção N_2. A argila calcinada tem a capacidade de remover o zinco de efluentes sintéticos. O modelo de Langmuir forneceu o melhor ajuste para as isotermas de sorção com uma quantidade máxima de metal adsorvida de 4,95 mg de metal g^{-1} de argila calcinada. Verificou-se que a adsorção foi fortemente influenciada pelas condições iniciais do processo e a adsorção foi confirmada pelas modificações das características físico-químicas da argila.
Palavras-chave: "Bofe", metal pesado, efluente.

Introduction

Numerous industrial activities have contributed to a significant increase in concentrations of metal ions in water resources due to the release of effluents. Conventionally, the removal of heavy metals takes place by chemical precipitation, but, although this process is relatively simple and inexpensive, generates a large volume of sludge and provides little benefit to very low concentrations of metals. In many situations the treated effluent may also contain residual concentrations of metals above the acceptable environmental conditions, requiring the application of a complementary process for polishing the final effluent.

The adsorption is reported as an alternative to tertiary treatment for removal of heavy metals in the opportunity to satisfactorily meet effluent with low concentrations of metals, in addition to using low cost adsorbents.

Alternative adsorbents such as natural clay have been assessed due to its high availability and cost-effectiveness for the removal of heavy metals. The use of clay as an adsorbent for removing heavy metals is due to its ion exchange capacity (CEC), selectivity, regenerability and abundance compared to other natural and synthetic adsorbents.

Studies such as those conducted by Jiang et al. (2010), Ghorbel-Abid et al. (2010), Vieira et al.

(2010), Silva et al. (2009), Fagundes-Klen et al. (2011) and Abollino et al. (2008) have investigated the potential of clays for the removal of heavy metals. Although the results involving metal removal by clays are significant and promising, the properties of adsorbents for optimizing the conditions of the process need to be better understood.

This paper evaluated the adsorption capacity of zinc on calcined Bofe clay in finite bath and the influence of parameters, such as adsorbent amount, pH and initial concentration of metal. The calcined Bofe clay (before and after zinc adsorption) was characterized by energy-dispersive X-ray spectroscopy, X-ray diffraction and N_2 physisorption.

Material and methods

Adsorbent

Bofe bentonite clay from Paraíba State, Brazil, was used as adsorbent. Clay was ground and its particles were separated by a sieving technique at 0.074 mm particle size. The natural clay was subjected to calcination process in a muffle furnace at 500°C for 24 hours. In the adsorption tests only calcined clay was used, because this clay is more stable, allowing its use in continuous systems.

Determination of point of zero charge of the adsorbent and metal chemical speciation

The point of zero charge of the adsorbent, pHzpc, was determined by potentiometric titration, according to Stumm (1992). This model shows that charges on the surface of the solid result from an acid-base reaction (Surface Complexation Model). The experimental procedure consisted of titrating two suspensions containing 10 g of clay each, in 100 mL of CH_3COONH_4 (0.1 M) as supporting electrolyte (after waiting 10 min. for stabilization of the sample), one containing CH_3COOH (0.3 M) and another containing NH_4OH (0.25 M). This titration was performed in a wide range of acid and base concentrations. The surface charge, Q in units of mol g^{-1}, was obtained by Eq. 1. The pHzpc value of the solid was obtained by building a chart of the total surface charge of the solid as a function of pH. This value corresponds to the pH in which the curve crosses the x-axis (Q = 0).

$$Q = \frac{C_a - C_b + [OH^-] - [H^+]}{C_S} \qquad (1)$$

Speciation diagrams of the distributions of zinc at 1.5 meq L^{-1} as a function of pH for the kind of Zn^{2+} were simulated using software HYDRA (*Hydrochemical Equilibrium - Constant Database*) in order to identify the different species in aqueous solution. These tests for determine the pH range in which the adsorption process predominates.

Adsorbent characterization

Calcined and contaminated clays were characterized by an Oxford 7060 X-ray spectroscopy system through dispersive energy (EDS), which enables qualitative evaluation of chemical composition. In order to indicate the mapping of the adsorbed metal on the Bofe clay, a scanning electron microscopy (SEM) at LEO equipment, LEO 440i, with 500 X power was performed. The specific surface area was obtained by N_2 physisorption in a Micromeritics Gemini III 2375 Surface Area Analyzer device using the BET method. The X-ray diffraction (XRD) for the basal spacing samples evaluation in Philips equipment, X'Pert model, Kα copper radiation (λ = 1.5418 Å), observing the diffraction angle of 2θ, step size of 0.02 degrees ranging between 4° and 50°.

Batch adsorption

The metal aqueous solution was prepared from salt of hexahydrated zinc nitrate, $Zn(NO_3)_2 \cdot 6H_2O$.

The adsorption experiments were carried out in finite bath with known amount of the adsorbent and 100 mL of solution metal at fixed concentrations of metal with pH = 4.5, defined according to metal speciation. The pH value of suspension was adjusted with dilute HNO_3 or NH_4OH. The erlenmeyers were kept at room temperature (25°C) under constant agitation (150 rpm). At predetermined intervals aliquots were taken and the metal concentration was determined in the ANALYST-100 Atomic Absorption Spectrophotometer. The adsorption capacity of metal ion at each time step was calculated by Eq. 2.

$$q_{eq} = \frac{V}{m_s}\left(C_0 - C_{eq}\right) \qquad (2)$$

where:

q_{eq} adsorption capacity of metal ion (mg g^{-1});

C_0 initial concentration of metal ion in solution (mg L^{-1});

C_{eq} final concentration of metal ion after reaching equilibrium (mg L^{-1});

V volume of solution (L);

m_s mass of adsorbent (g).

The effect of the contact time, pH of the adsorbate solution, adsorbent amount and adsorbate

concentration on the kinetics of zinc were studied. The experimental procedure mentioned above was used, with some changes depending on the parameter studied.

(a) Effect of contact time: 1 g of clay 100 mL^{-1} of zinc solution (100 mg L^{-1}), interaction time 300 min., pH 4.5, 25°C.

(b) Effect of initial solution pH: 1 g of clay 100 mL^{-1} of zinc solution (100 mg L^{-1}), interaction time 150 min., pH range of 2-10, adjusted before starting the adsorption experiments.

(c) Effect of adsorbent amount on metal ion adsorption: 100 mL of zinc solution (100 mg L^{-1}) with different adsorbent amounts (0.5, 1.0, 2.0, 3.0 and 4.0 g), interaction time 150 min., pH 4.5, 25 °C.

Equilibrium tests were performed with 1 g of clay 100 mL^{-1} of zinc solution, adsorbate concentration varying from 3.0 to 200 mg L^{-1}, interaction time 150 min., pH 4.5, 25°C. The experimental data were fitted with Langmuir (Eq. 3) and Freundlich (Eq. 5) isotherms. The fitting was performed using software Origin 6.0.

$$q_{eq} = \frac{q_m b C_{eq}}{1 + b C_{eq}} \tag{3}$$

where:

q_m maximum amount of ion adsorbed per unit of adsorbent mass to form a complete monolayer on the surface, (mg g^{-1});

b constant related to adsorption energy, corresponds to the affinity between adsorbent surface and solute, (L mg^{-1}).

The essential characteristics of Langmuir isotherm can be expressed by the constant dimensionless number, separation factor or equilibrium parameter (R_L), which indicates the curvature of the sorption isotherm: if $R_L > 1$, the isotherm is not favorable; if $R_L = 1$, it is linear; $0 < R_L < 1$, favorable; $R_L = 0$, irreversible. This value is given by Eq. 4:

$$R_L = \frac{1}{1 + b C_0} \tag{4}$$

$$q_{eq} = K_f \cdot C_{eq}{}^n \tag{5}$$

where:

k_f constant related to adsorbent capacity;
n constant related to adsorption intensity.

Results and discussion

pH$_{ZPC}$ and zinc speciation

The electrical charge of clay surfaces is dependent on pH. There is a particular pH value where the amounts of positive and negative electric charges are equal, this pH value, typical of each clay, is called point of zero charge pHzpc. The main surface functional groups in clays that generate loads are pH-dependent Si-OH groups and Al-OH.

Figure 1 (a) shows the pHzpc of the clays. The values of pH$_{ZPC}$ obtained for the natural and calcined clays are, respectively, 6.0 and 5.3. This difference is because there are more hydroxyl groups in natural clays, while in calcined clay the dehydroxylation occurs with the calcination process. Thus the adsorption should be made in a pH range > pHzpc, in this case pH > 5.3 for the calcined clay.

The objective was to maximize the removal of zinc ions from an aqueous solution, considering that the ion behaves as a cation, thus it was decided that the adsorption process would be conducted in a range of pH > pHzpc in this case, pH > 5.3 for the calcined clay. However, in view of the effect of precipitation of Zn^{2+} at high pH values was made a study of chemical speciation of this ion at 1.5 meq L^{-1} as a function of pH (Figure 1b). The pH for this study was defined by the outcome of the two procedures, i.e. by pH$_{ZPC}$ and chemical speciation of the ion. According to Figure 1 (b) at pH 5.0 to 9.0, and pH above 7.0, the fraction of Zn^{2+} in aqueous solution decreases and starts the formation of ZnOH$^+$ and Zn(O). It is known that metal species are present in deionized water in the forms of Zn^{2+}, ZnOH$^+$, Zn(O) and Zn(OH)$_{2(S)}$. Within the pH range of 1.0 - 5.0, the solubility of the Zn(OH)$_{2(S)}$ is high and therefore, the Zn^{2+} is the main species in the solution. Within the pH range of 5.0 - 9.0 the solubility of Zn(OH)2(S) decreases and at pH ~10.0, the solubility of Zn(OH)2(S) is very low. At this time, the main species in the solution is Zn(OH)2(S) and the fraction of ions Zn2+ in aqueous solution decreases.

By analysis of pH$_{ZPC}$, the adsorption should be performed in a pH range > pHzpc, in this case, pH > 5.3. However the chemical speciation at pH = 5.0 starts the precipitation of zinc. Thus, to ensure the process of adsorption, the pH was set at 4.5 in all conditions studied in this work.

The pH of the dispersion formed by natural and calcined Bofe clay was measured directly, in which 1 g of clay was dispersed in 100 mL of deionized water. The results were pH of 7.7 and 4.3 for the natural and calcined Bofe clay, respectively.
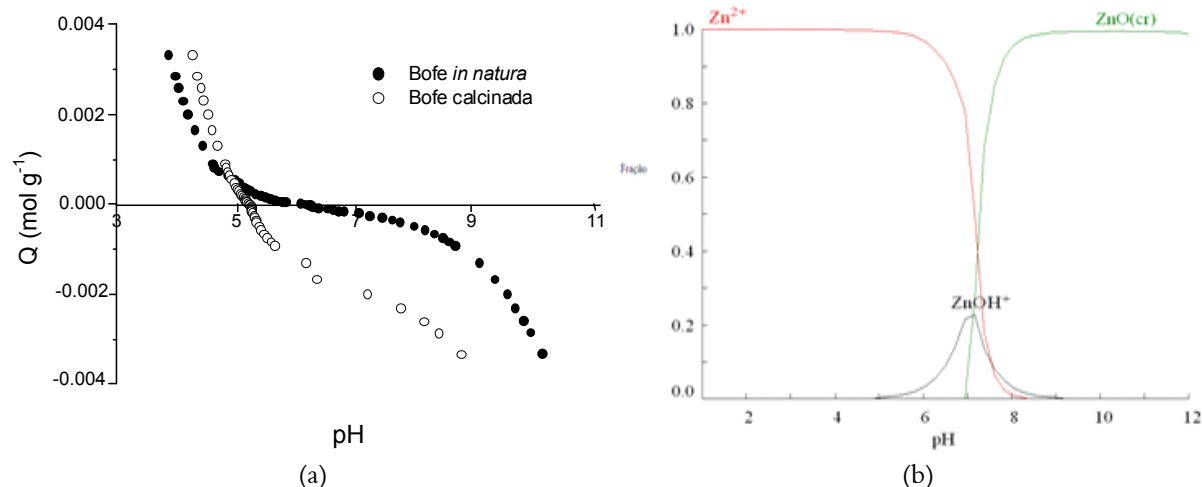
(a)   (b)

Figure 1. (a) pHzpc of natural and calcined clays. (b) Zn^{2+} speciation curve.

The pH of the clay results in part from the nature of exchangeable ions present. According to the chemical composition obtained by EDS (Table 1), the ions exchangeable of Bofe clays are alkali metal cations and alkaline earth metals, which give an alkaline pH to the dispersions formed by natural clays. With calcination, there is no loss of cations, but dehydroxylation, which gives an acid pH for the dispersion formed by the calcined clay.

Characterization of clay samples

Qualitative chemical analysis of the clays is listed in Table 1. All elements in the average composition have a percentage within the expected for this clay, according to Souza Santos (1992). There is predominance of Si and Al, basic elements for smectite clay group. Bofe clay can be designated as a polycationic bentonite due to the presence of Ca^{2+}, Mg^{2+} and Na^+ cations. The contents of these exchangeable cations are interesting for the adsorption process. This type of clay is the most frequently found in Brazil (AMORIM et al., 2006).

Table 1. Chemical analysis of the clays.

Components (% mass)	Calcined	Calcined + Zn
Na	0.50	-
Mg	1.19	1.10
Al	6.84	6.41
Si	46.17	36.87
K	-	-
Ca	0.58	0.38
Ti	0.53	0.40
Fe	3.32	3.55
Zn	-	0.67
Total	59.13	49.38

The presence of zinc after adsorption shows that this metal was actually adsorbed by clay. With the zinc adsorption, there was a reduction in the

amount of Ca^{2+} and Mg^{2+} cations and disappearance of Na^+ cations, indicating the occurrence of ion exchange, especially with Na^+. Figure 2 shows a homogeneous distribution of metal adsorbed on the clay surface.
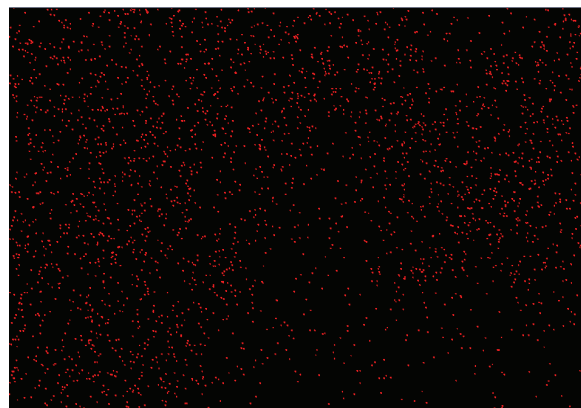

Figure 2. Metal mapping on Bofe calcined clay with 1000 X magnification.

The values obtained for the specific surface area by the BET method for calcined and contaminated Bofe clays are presented in Table 2. The BET method was chosen because presents the best fit of data, when compared to those of the Langmuir model, in addition to the similar behavior of the curves obtained with BET isotherms.

The N_2 adsorption analysis includes only the external surface area of bentonite clay. According to Yukselen et al. (2006), the N_2 adsorption method is performed under dry conditions, where the layer of the montmorillonite (bentonite) is tightly bound. Thus, the molecules of the selected gas cannot cover the interlayer surfaces. In the calcined clay occurs a structural change due to

thermal treatment affecting the interaction with water of exchangeable ions present between the clay layers, so that calcined clay does not expand, and its area measured by N_2 adsorption adequately represents the clay.

Table 2. Specific surface area and volume pores of clays by BET method.

Samples	Specific Surface Area ($m^2 g^{-1}$)	R^2
Calcined	89.02	0.9997
Calcined + Zn	41.74	0.997

The specific surface area of clay decreased after the zinc adsorption because Zn^{2+} ions occupied the active sites of clay that would be available for N_2, blocking the area and preventing the passage of molecules. XRD analysis confirms this blockade, Figure 3.

The diffractograms obtained for calcined and contaminated bentonite clay samples are shown in Figure 3. Thus, it is possible to observe the presence of montmorillonite and quartz, typical of this type of clay whereby smectite is the predominant clay mineral (SOUZA SANTOS, 1992). Thermal treatment caused distortions in the crystalline structure modifying thus the Bragg reflection standards, calcination may be followed by cation movement within the octahedral sheet (BOJEMUELLER et al., 2001). The contaminated clay has a mangling of peak d(001) due to Zn^{2+} adsorption that replaces the exchangeable cations interlayer.

Adsorption experiments

(a) Effect of contact time and adsorption kinetics
Experiments were performed to evaluate the behavior of the kinetics of zinc removal by calcined clay. Figure 4 presents the adsorption kinetics of zinc at an initial concentration of 100 mg L^{-1} on calcined clay.
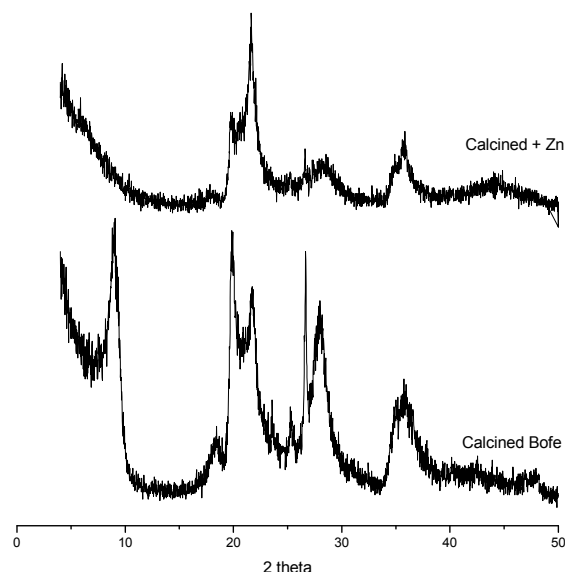

Figure 3. Calcined and calcined + Zn Bofe clays diffractograms.

The adsorption of zinc ions into clay pores occurs rapidly at the first moments of the process where there are a lot of empty sites for adsorption, and over time, the number of empty sites decreases and favors the action of repulsive forces of molecules already adsorbed zinc, which complicates the process of adsorption by the remaining sites (STATHI et al., 2007). The maximum adsorbed amount was 4.95 mg metal g^{-1} clay (Figure 4a). The reduction in the concentration of zinc ions under the condition of this study was 56% compared to the initial concentration of 100 mg L^{-1} (Figure 4b).
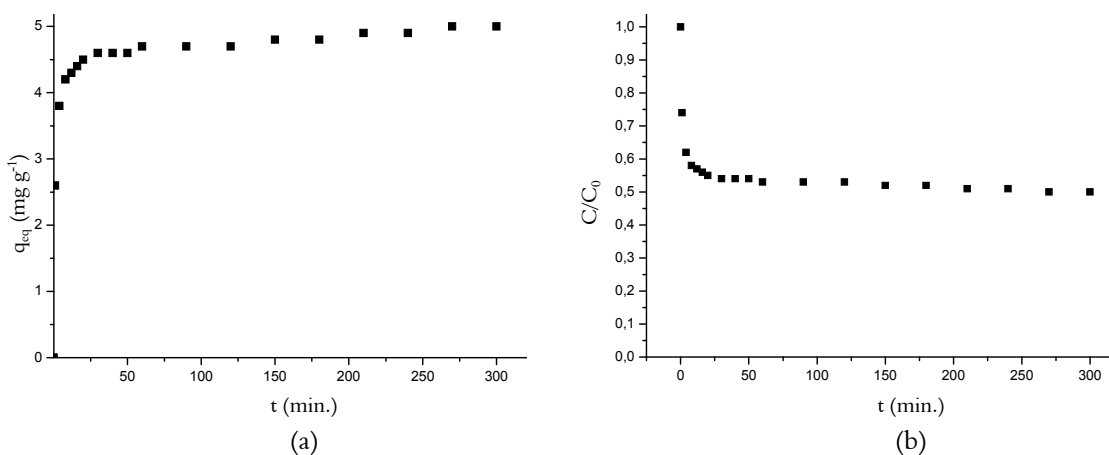

(a)

(b)

Figure 4. Kinetic curve for zinc adsorption on calcined clay. (a) Adsorbed amount at equilibrium; (b) dimensionless solution concentration as a function of adsorption time.

(b) Effect of initial solution pH

Several studies such as Abollino et al. (2008), Chen et al. (2008), Arias and Sen (2009) observed that the solution pH is an important parameter in the adsorption of metal ions on clay. Very high values of metal solutions pH should be avoided because they may cause precipitation of metal complexes and hinder the distinction between adsorption and precipitation as metal removal process. The solution pH affects the loads on the adsorbent surface, but also influences the ionization of the solute, or interferes with ions (KUBILAY et al., 2007).

Figure 5 shows the influence of solution pH on removal of zinc ions by Zn^{2+} calcined clay. There was an increase of metal removal with increasing pH of the adsorbate. In the pH range between 2 and 5 the removal process probably occurred by adsorption. In the range of 5 to 8, there was a marked increase in the amount of zinc removed, but, this pH range began to form $ZnOH^+$ decreasing the fraction of Zn^{2+} in aqueous solution. At pH above 8.0, there was a further increase in the removal of zinc as a result of chemical precipitation of metal in the form of zinc hydroxide, as noted in the study of chemical speciation (Figure 1b). Therefore, an optimum pH for the adsorption of Zn^{2+} in aqueous solution at 100 mg L^{-1} should be below 5.0, this value being consistent with the study of chemical speciation of zinc.
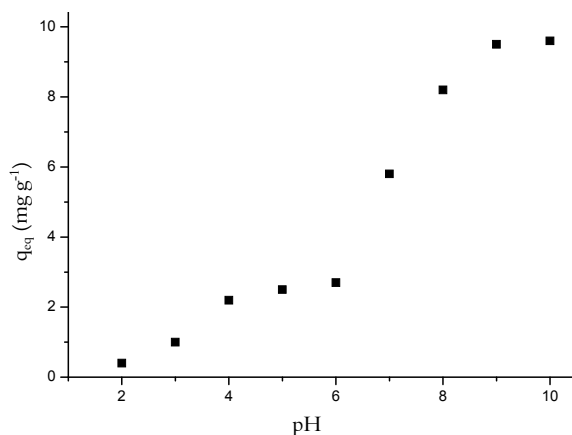

Figure 5. Effect of solution pH on Zn^{2+} removal on calcined clay.

(c) Effect of adsorbent amount on metal ion adsorption

The results of the kinetic experiments with varying adsorbent concentrations are presented in Figure 6. The amount of Zn^{2+} adsorbed per unit mass of adsorbent decreased as the adsorbent mass increased. The decrease in the amount adsorbed per

unit weight of adsorbent is a common behavior also reported by Bhattacharyya and Gupta (2008). This fact probably occurred because a greater amount of adsorbent reduces the unsaturation of adsorption sites and hence the number of sites per unit mass decreases, resulting in a lower adsorption rate to a greater amount of adsorbent.
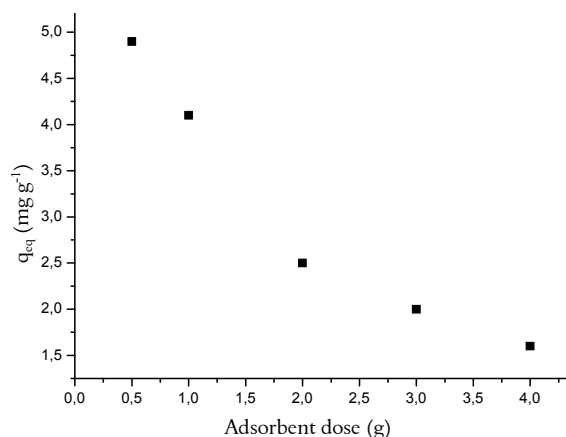

Figure 6. Effect of the adsorbent amount on adsorption capacity.

(d) Effect of adsorbate concentration and adsorption isotherm

The adsorption of the Zn^{2+} ion by calcined clay is described by Langmuir and Freundlich isotherms (Figure 7). The isotherms showed basically the same behavior, and can be classified as favorable. Table 3 lists the parameters obtained through these adjustments.
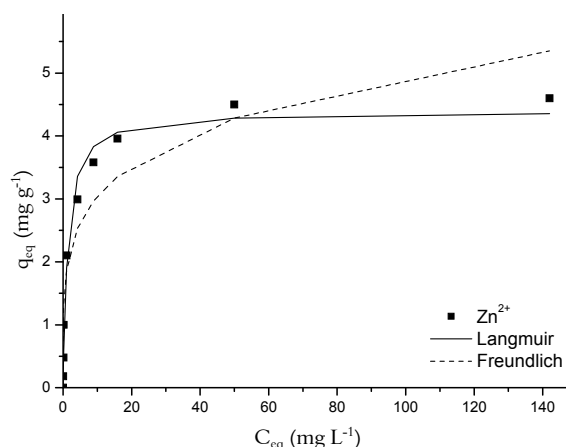

Figure 7. Adsorption isotherms adjusted to the models of Langmuir and Freundlich.

Table 3. Ion Zn^{2+} parameters obtained by fitting the models of Langmuir and Freundlich.

Bofe clay	Langmuir			Freundlich		
	q_m (mg g^{-1})	b (L mg^{-1})	R^2	k_f (L g^{-1})	n	R^2
calcined	4.395	0.767	0.9822	18.663	0.213	0.9459

By the R^2 values in Table 3, it is possible to note that Langmuir model best fits the concentrations of Zn^{2+} adsorbed. Similar results were found by Bhattacharyya and Gupta (2007) for the removal of heavy metals on montmorillonite and by Tito et al. (2008) for the removal of Zn^{2+} on bentonite clay. The values for Freundlich constant is around 0.3 indicating that the adsorptive characteristics of calcined and sodium-saturated Bofe clays are good for zinc adsorption (TREYBAL, 1980). The amount of metal adsorbed at equilibrium, adjusted by Langmuir model, was 4.4 mg g^{-1}.

To evaluate the affinity between adsorbate and adsorbent, the dimensionless separation factor (R_L) was calculated, based on Langmuir constant b and the initial zinc concentration presented in Table 4. The values of R_L for zinc adsorption on calcined clay ranged between 0 and 1, characterizing a favorable adsorption, mainly for the highest initial concentrations of metal.

Table 4. Separation factor values (R_L) for Zn^{2+} adsorption by calcined Bofe clay.

C_0	R_L
1.92	0.41
4.9	0.21
10.2	0.11
22	0.06
34.1	0.04
44.7	0.03
55.5	0.03
95	0.01
188	0.01

Conclusion

Calcined Bofe clays presented adequate capacity of adsorption of Zn^{2+} in aqueous solution under the study conditions, and can replace other adsorbents more expensive due to its high availability and good adsorption properties. The characterization demonstrated the changes occurred in the clays after the zinc adsorption thus proving that the process occurred by ionic zinc exchange with intermellar cations. The experimental data at equilibrium satisfactorily fitted the Langmuir model.

Acknowledgments

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