

# COMPETITIVE ADSORPTION KINETICS AND EQUILIBRIUM OF ZINC AND COPPER IONS IN EXPANDED VERMICULITE

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**ABSTRACT:** Industrial effluents represent the main resource of pollution of soil and water with heavy metals. These elements are extremely dangerous in high concentrations to fauna and flora, because they are bio accumulated in living organisms. Then, many removal techniques have been studied to optimize the waste treatment, aggregating low cost to great removal capacity. This work aims to investigate adsorption process of binary system of zinc and copper ions onto expanded vermiculite, an alternative adsorbent material, through kinetics experiments and isotherms at 293 K, 313 K and 333K. Furthermore, kinetics curves were predicted by Intraparticle Diffusion, Pseudo first-order and Pseudo second-order models. Equilibrium data were fitted by Langmuir and Langmuir-Freundlich's model. This adsorption process demonstrated to be spontaneous, favorable, endothermic and more selective for copper ions.

**KEYWORDS:** adsorption; expanded vermiculite; heavy metal removal; binary system.

## 1. INTRODUCTION

Heavy metals as zinc and copper are a significant source of contamination of soil and water resources, since they are bioaccumulated along the food chain and extremely dangerous to fauna and flora when their concentrations exceed the established limits set by the current legislation. Metal ions are present mainly in liquid waste generated by industrial processes (Derísio, 2005). As a result, the waste/effluents management politic objectifies to prevent and to minimize the pollution of water resources, mitigating potential damages to aquatic environment (Péric, 2005).

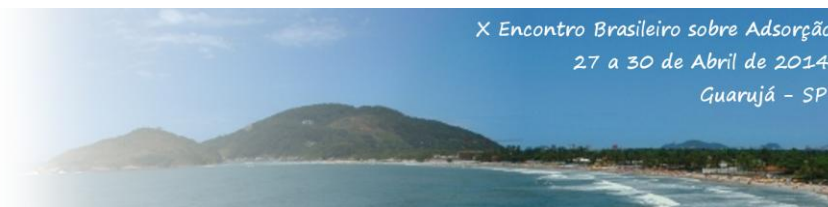
Zinc is beneficial to human metabolism in small amounts, contributing in catalytic, structural and regulatory functions. In big quantities, it can cause poisoning, nausea and diarrhea (Maret and Sandstead, 2006). In plant, it can cause troubles in transpiration, photosynthesis and enzyme activity.

Copper is a fundamental element present in the process of blood generation and in use of iron, with diary requirement of 0,03 mg/kg to adults (Alloway, 1990). Its extreme can originate many diseases, like gastric ulcer, liver necrosis and renal troubles. To fishes, it's the second most toxic heavy metal.

Cu (II) and Zn (II) are found naturally in the water, animals and plants, but their increase must be controlled. The permitted concentration limited of zinc effluent discharge in superficial waters is 5 mg/L, whereas to copper, it is 1 mg/L (CONAMA Resolution, 2011).

Conventional biological treatments do not remove heavy metals from industrials effluents. Among the techniques used, there are physico-chemical precipitation, ion exchange and solvent extraction. However, these traditional methods have low efficiency to separate big amounts of effluents in low concentrations of metals (Chui, 2005). To optimize the wastewater treatment process, alternatives techniques have been developed, trying to aggregate low cost raw materials with high pollutant-removal efficiency. The adsorption process is receiving more attention because it is inexpensive, simple, versatile and particularly effective at low concentrations (Nishikawa et al, 2012a; El-Bayaa et al, 2009).

Vermiculite is a mineral clay with promising potential of adsorption (Nishikawa et al., 2012; Alexandre-Franco et al., 2011; Fonseca et al., 2005; Fonseca et al., 2006). Composed by layer silicates, this micaceous material presents a cation-exchange capacity (CEC) from 100 to 150



meq/100g of clay (Chui, 2005). Its exfoliated form is weightless, more refractory and chemically inert (Franco et al, 2001). Previous study that investigated the adsorption of Cu(II), Zn(II), Pb(II) and Cr(II) by Brazilian expanded vermiculite in single solutions indicated the adsorbent material's higher affinity by ions  $Zn^{+2}$  than by ions  $Cu^{+2}$  (Nishikawa et al., 2012). In this work, the adsorption process of binary systems (Cu(II) and Zn(II)) onto expanded vermiculite was analyzed through kinetics and equilibrium studies.

## 2. MATERIALS AND METHODS

### 2.1 Adsorbent

Vermiculite is a micaceous material composed of  $SiO_4$  tetrahedral layers,  $Mg(OH)_2$  and  $Al(OH)_3$  octahedral layers. Its crystalline structure has 5-20% of inter-layer water and can be exfoliate by heating. By exfoliation, vermiculite loses water molecules, increasing its volume around 20 times and decreasing its density between 0.05 and 0.30  $g\ cm^{-3}$  (Machado et al., 2006).

The expanded vermiculite used in this study was supplied by Brasil Minérios. The material was triturated and sifted to obtain a particles with Sauter diameter about 0.855 mm. In a characterization study of the same commercial adsorbent, Nishikawa et al. (2012a) found out the general formula provided in literature  $[(Si_3Al)Mg_3(OH)_2O_{10}.Mg_{0.5}.nH_2O]$ , besides small amounts of chromium and titanium. In that study, the volume obtained by helium pycnometry was 0.8935  $cm^3$ , the real density was 2.4644  $g/cm^3$ , the superficial area estimated by  $N_2$  physisorption was 22.2353  $m^2/g$  and the Cation Exchange Capacity (CEC) obtained was approximately 445 meq/100 g of expanded vermiculite.

### 2.2 Metal Speciation

The intersection of pH interval in which chemical precipitation does not occur for both metals was determined by metal speciation provided by HYDRA software (Puigdomenech, 2004).

### 2.3 Copper and zinc solutions

Copper and zinc solutions were prepared from copper nitrate ( $Cu(NO_3)_{2.3}H_2O$ ) and zinc nitrate ( $Zn(NO_3)_{2.6}H_2O$ ) salts, respectively, dissolved in distilled and deionized water.

### 2.4 Kinetics curves

Bicomponent kinetics experiments in batch were carried out with solutions at different concentrations, in room temperature (298 K), for 360 minutes. Around 100 g of vermiculite and 1000 mL of solution was remained in Erlenmeyer, under constant agitation. The pH was monitored using pHmeter and controlled with nitric acid. At pre-set times, aliquots with 4 mL of solution were withdrew by automatic pipette. Thus, the volume reduction did not surpass 8% of total volume and did not influence the solution concentration during the essay. These aliquots were centrifuged for 10 min at 40 rpm. Then, they were diluted and analyzed in atomic absorption Shimadzu, type AA-7000. Copper and zinc initial concentrations used in the kinetics experiments were, respectively: 0.44 mmol/L and 0.44 mmol/L; 0.20 mmol/L and 0.54 mmol/L; 0.74 mmol/L and 0.58 mmol/L.

The ion concentration adsorbed in the vermiculite,  $q$  (mmol/g), could be calculated by Equation 1, in mmol/g:

$$q(t) = \frac{V}{m} (C_0 - C(t)) \quad (1)$$

where  $C_0$  is the metal ions' initial concentration (mmol/L),  $C(t)$  is the metal ion concentration in solution at time  $t$  (mmol/L),  $V$  is the solution volume and  $m$  is the mass of dry vermiculite (g). As a result, in  $t=0$ , the ion concentration in the solid is zero.

Three mathematical models were employed to adjust kinetics curves, each one based on a different mechanism of mass transference (Almeida Neto, 2011). In pseudo first-order model, the resistance of mass transference in the solid prevails. It is represented by Equation 2:

$$q(t) = q_e (1 - e^{-k_1 t}) \quad (2)$$

where  $q_e$  is the concentration of metal ion in the solid in the equilibrium time (mmol/g) and  $k_1$  is the kinetic constant of removal ( $min^{-1}$ ).

Cases in which the kinetic system follows a behavior of non-linear impeller forces, the curve is adjusted by pseudo second-order model, represented by Equation 3:

$$q(t) = \frac{k_2 \times q_e \times t}{(1 + k_2 \times t)} \quad (3)$$



where  $k_2$  ( $\text{min}^{-1}$ ) is the kinetic constant of second-order multiplied ( $\text{g}/\text{mmol}\cdot\text{min}$ ) by  $q_e$  ( $\text{mmol}/\text{g}$ ).

The intraparticle diffusion model describes the adsorption process in three or more stages: instantaneous adsorption in external surface; gradual intraparticle diffusion, represented by Equation 5; and the equilibrium stage, when the adsorption decreases.

$$q(t) = k_i \times t^{1/2} + c \quad (4)$$

where  $k_i$  is the angular coefficient of the straight provided by the graphics  $q(t)$  versus  $t^{1/2}$ , in  $\text{mmol}/\text{g}\cdot\text{min}^{1/2}$ , whereas the constant  $c$  is the linear coefficient ( $\text{mmol}/\text{g}$ ).

## 2.5 Equilibrium isotherms

The investigation about temperature influences was performed by isotherm experiments in 293 K, 313 K and 333 K. Erlenmeyers containing 0.5 g of expanded vermiculite and 50 mL of zinc and copper solution in different proportions remained in shaker with temperature and agitation control for 6 h. Aliquots of the solutions were centrifuged, diluted and analyzed in atomic absorption as well as for initial concentrations.

Langmuir and Langmuir-Freundlich equilibrium models to binary adsorption systems were used for mathematical prediction. They are represented by Equations 5 and 6, respectively.

$$q_{e,i} = \frac{q_m \times b_i \times C_{e,i}}{1 + (b_i \times C_{e,i} + b_j \times C_{e,j})} \quad (5)$$

$$q_{e,i} = \frac{q_m \times k_i \times C_{e,i}^{n_i}}{1 + (k_i \times C_{e,i}^{n_i} + k_j \times C_{e,j}^{n_j})} \quad (6)$$

In both equations,  $i$  and  $j$  are the number of components,  $q_e$  is the adsorbed quantity onto the solid phase ( $\text{mmol}/\text{g}$ ),  $C_e$  is the equilibrium concentration of the solute in the fluid phase ( $\text{mmol}/\text{L}$ ) and  $q_m$  is the maximum quantity of adsorbed ions ( $\text{mmol}/\text{g}$ ) in the clay. In Equation 5,  $b$  is the Langmuir equilibrium constant of adsorption ( $\text{L}/\text{mmol}$ ). The Equation 6 represents an union of Langmuir model to the Freundlich model,

proposed by Sips (1948). The parameters  $k$  and  $n$  (dimensionless) correspond to the empirical constants of Freundlich.

## 3. RESULTS AND DISCUSSION

Figure 1 (A – F) shows the diagrams of metal speciation to the binary systems for kinetic and isotherm experiments. The theoretical concentrations of zinc and copper analyzed in speciation were, respectively: 0.5  $\text{mmol}/\text{L}$  and 0.5  $\text{mmol}/\text{L}$ ; 1  $\text{mmol}/\text{L}$  and 2  $\text{mmol}/\text{L}$ ; 2  $\text{mmol}/\text{L}$  and 1  $\text{mmol}/\text{L}$ .

From Figure 1 it can be seen that  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  fractions occur in pH below 5, so the pH during the experiments was maintained below 4,5 to avoid chemical precipitation.

Kinetic experiments were carried out in different proportions of the metals to investigate their affinity and selectivity with the expanded vermiculite. The adsorption curves and the kinetic models' fits are shown in Figure 2 (A - C).

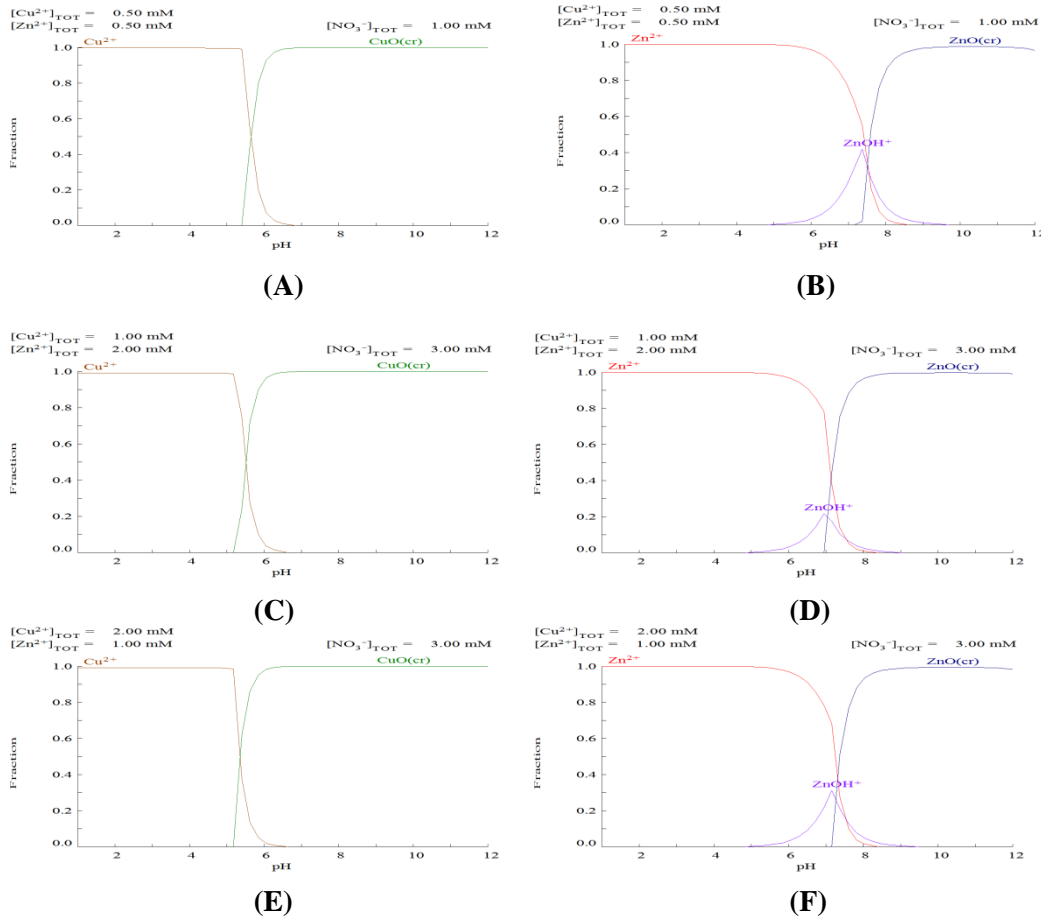
As can be noticed, all curves reached equilibrium stage under 120 minutes. This result is comparable to that obtained in single systems with zinc and other metals reported by Nishikawa et al. (2012a, 2012b). Although, in single system (Nishikawa et al. 2012b), the vermiculite showed higher affinity with zinc ions than copper ions, while Figure 2 (A) indicates higher selectivity of  $\text{Cu}^{2+}$  in equimolar presence of  $\text{Zn}^{2+}$  ions. Figures 2 (B) and (C) evidence that adsorption process is directly proportional to solute concentration.

The kinetic models provided a good fit of adsorption curves, as can be seen by the coefficients of determination,  $R^2$ , shown in Table 1. This table also contains the removal rates constants  $k_i$ ,  $k_1$  and  $k_2$  from intraparticle diffusion, pseudo-first order and pseudo-second order's models, respectively, besides the quantity of metal ion adsorbed onto the solid in the equilibrium,  $q_e$ . The intraparticle diffusion fits did not present the instantaneous adsorption in external surface, indicating that the gradual intraparticle diffusion can be a limiting stage of the process. Their removal constants,  $k_i$ , showed higher values to the prevalent metal in the solution; in equimolar solution, copper got the higher  $k_i$  value, evidencing its higher selectivity. When zinc was in largest proportion, as Kinetic B of Table 1, intraparticle diffusion model fitted better the kinetic data; whereas for the other cases, the best mathematical



fit was the pseudo second-order model, because its coefficients of determination were closer to 1 and the  $q_e$ 's values were more consistent with the

empirical values if compared to pseudo first-order values.



**Figure 1.** (A) (C) (E) Metal speciation of copper. (B) (D) (F) Metal speciation of zinc.

Kinetic experiments of the expanded vermiculite as adsorbent indicated an efficiency about 83% and 68% to remove zinc and copper (in binary system), respectively, from aqueous solution at low concentrations.

Figure 3 (A – C) shows the adsorption isotherms and their mathematical prediction by Langmuir (L) and Langmuir-Freundlich (LF)'s models. The parameters and coefficients of determination obtained from these equilibrium models are shown in Table 2. Both models fitted the experiments reasonably well, especially the second one. Although not thermodynamically consistent, LF model had also been shown to provide a good empirical correlation of binary equilibrium data of number of simple gases on molecular sieve adsorbents and single equilibrium data of organic compounds onto alternative

adsorbent (Souza, 2013; Ruthven, 1938). In this model, represented by Equation 6, Langmuir's equation was united to Freundlich's model of potency to better represent the results of adsorption, especially onto heterogeneous solids (Souza, 2013). The  $k$ 's constant is related to maximum quantity of ions onto stationary phase.

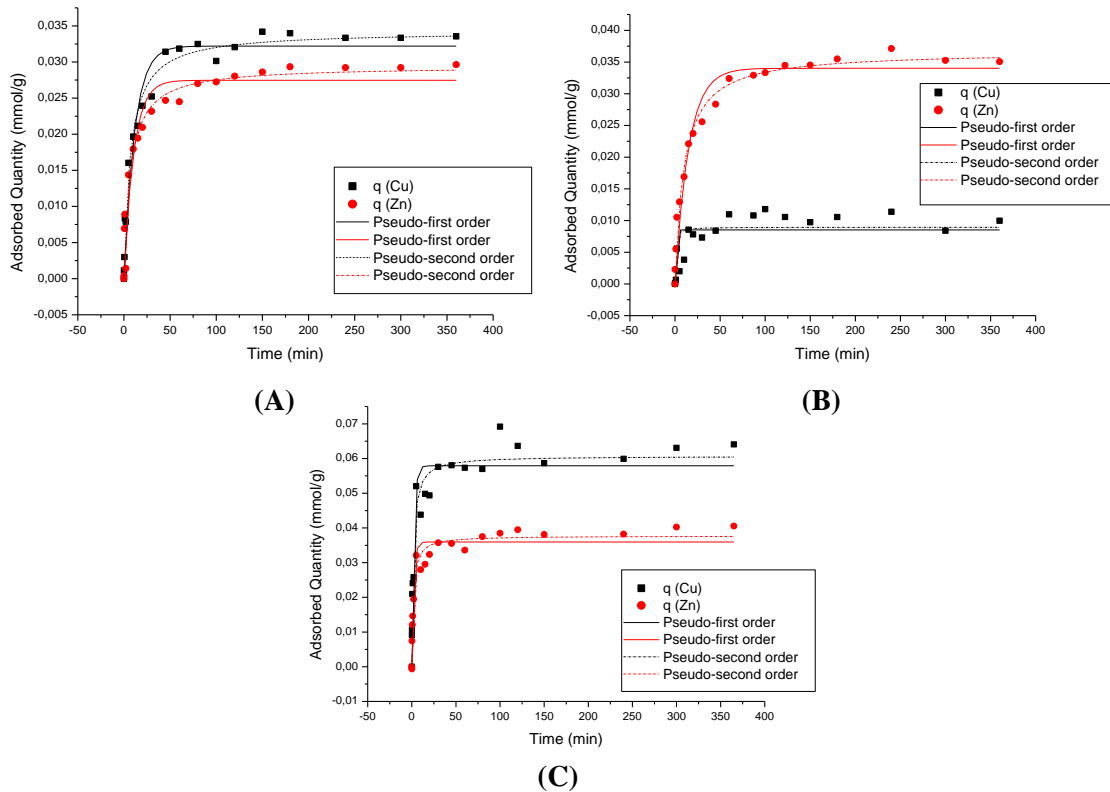
From Figure 3 (B), it can be noticed that the adsorption process of  $Zn^{2+}$  in presence of  $Cu^{2+}$  ions, at 313 K, resembles the isotherm predicted by Henry's law. For both metallic ions, the biggest adsorbed quantity presenting the lowest final concentration in fluid phase occurred at 333K. This result indicates the endothermic nature of the system and can be explained by the increase in surface area of the stationary phase that expands due to the temperature. This temperature's influence reflects the high value of maximum



adsorbed quantity,  $q_m$ , observed at higher temperature.

Figure 3 (A) and 3 (C) demonstrate clearly the higher selectivity for the adsorption of copper onto expanded vermiculite, as kinetic experiments did. The  $b$ 's parameter obtained from the Langmuir's fit also evidences this property,

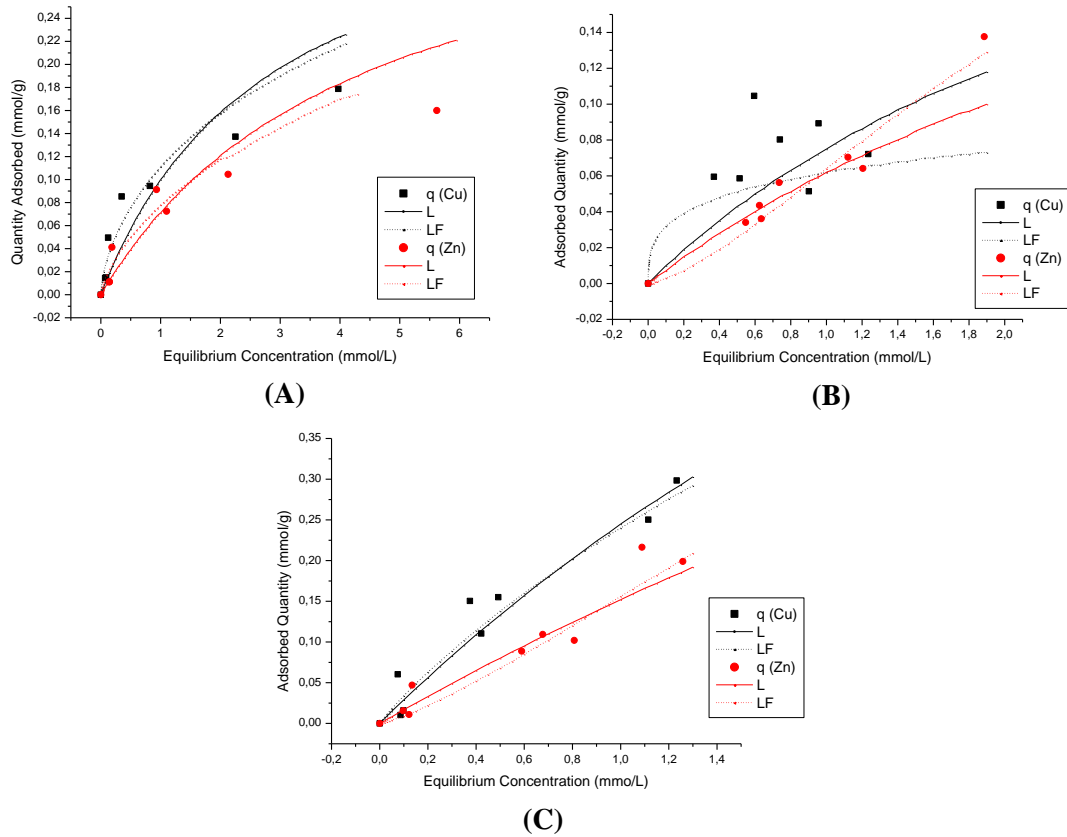
because it showed greater values to copper at all experimental temperatures. According to Bhattacharyya and Gupta (2007), this constant represents the ratio between the rates of adsorption and desorption, i. e., high values of the parameter  $b$  indicate strong affinity of ion by the solid sites.



**Figure 2.** Non-linear fits of kinetics curves with Cu(II) and Zn(II), respectively, at initial concentrations: (A) 0.44 and 0.44 mmol/L; (B) 0.20 and 0.54 mmol/L; (C) 0.74 and 0.58 mmol/L.

**Table 1.** Parameters and coefficients of determination of kinetic models for adsorption of zinc and copper onto vermiculite,  $k_i$  in  $\text{mmol/g}\cdot\text{min}^{1/2}$ ,  $c$  in  $\text{mmol/g}$ ,  $q_e$  in  $\text{mmol/g}$ ,  $k_1$  and  $k_2$  in  $\text{min}^{-1}$ .

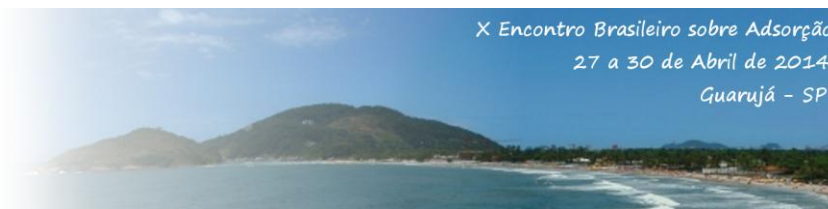
Kinetic	Metal	Intraparticle Diffusion			Pseudo-first Order			Pseudo-second Order		
		$k_i$	$c$	$R^2$	$k_1$	$q_e$	$R^2$	$k_2$	$q_e$	$R^2$
A	Copper	0.0047	0.0018	0.9783	0.0876	0.0322	0.9598	0.1442	0.0342	0.9837
	Zinc	0.0039	0.0021	0.9368	0.0957	0.0275	0.9300	0.1445	0.0294	0.9564
B	Copper	0.0014	0.0005	0.9075	0.0693	0.0103	0.8707	0.1126	0.0110	0.8712
	Zinc	0.0042	0.0027	0.9809	0.0662	0.0340	0.9584	0.1011	0.0367	0.9844
C	Copper	0.0098	0.0107	0.9184	0.4318	0.0579	0.9065	0.5924	0.0607	0.9442
	Zinc	0.0064	0.0057	0.9074	0.4755	0.0360	0.9318	0.6224	0.0377	0.9698



**Figure 3.** Langmuir (L) and Langmuir-Freundlich (LF)'s mathematical prediction of binary adsorption isotherms at the temperatures: (A) 293 K, (B) 313 K e (C) 333 K.

**Table 2.** Parameters and coefficients of determination of equilibrium models for adsorption of zinc and copper onto vermiculite.

Model	Parameter	293 K		313 K		333 K	
		Copper	Zinc	Copper	Zinc	Copper	Zinc
L	$q_m$ (mmol/g)	0.3838		0.3246		1.4638	
	b (L/mmol)	0.6177	0.4035	0.5225	0.3866	0.2385	0.1501
	$R^2$	0.9591	0.9850	0.7650	0.9347	0.9729	0.9719
LF	$q_m$ (mmol/g)	0.6596		0.3523		1.4529	
	k	0.2570	0.1725	0.3847	0.3130	0.2392	0.1547
	n	0.6314	0.7027	0.3259	1.4872	0.9185	1.2895
	$R^2$	0.9752	0.9836	0.8855	0.9738	0.9732	0.9799



The metal affinity and selectivity sequences of clays are normally associated with the metal physicochemical properties and the clay peculiarities. Padilha-Ortega et al (2013), in their study about binary adsorption of heavy metals onto vermiculite, sepiolite and bentonite, reported that affinity sequence is dependent upon the softness and ionic radius of the metal cations. In this case, copper is more softness than zinc ( $\text{Cu } 2.89 > \text{Zn } 2.34$ ), but the ionic radius of them are too close and probably are not meaning when these ions compete for the same sites.

The greater selectivity of copper ions in binary system despite the higher affinity of zinc ions in single system can be explained by the speed of water ligands attaching and detaching each metal's aqua complex. Both cations form octahedral complexes with water molecules, however, copper exhibits the fastest water exchange rate (Helm and Merbach, 2005). In the competition,  $\text{Cu}^{2+}$  can break its chemical ligands with water and set them with the adsorbent faster, ensuring its largest adsorption.

## 4. CONCLUSIONS

Equilibrium studies as well as kinetic experiments demonstrated the good removal capacity of heavy metals by Brazilian expanded vermiculite, reaching 83% and 68% for copper and zinc, respectively, in mixture. Considering the low adsorbent cost and the simplicity of adsorption process, the results indicate that expanded vermiculite is a promising adsorbent of binary heavy metals solutions.

Earlier study demonstrate higher affinity of zinc ions in single system (Nishikawa et al., 2012b), but in binary system a greater selectivity of copper ions was verified. This behavior probably can be justified by the physicochemical metals properties, since  $\text{Cu}^{2+}$  is more softness and has a faster water exchange. From the equilibrium study, it could be noticed the natural endothermic aspect of this adsorption process, showing an increase in adsorbed quantity of ion at higher temperature (333 K).

The numerical models to predict kinetic curves and equilibrium data provided good fit and correlation to empirical values. Intraparticle diffusion and pseudo second-order's models can be evidenced for kinetic curves, and Langmuir-Freundlich's model for equilibrium data.

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