

Removal of Heavy Metals in K-Bentonite Clay

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This work aimed to investigate the removal of Pb(II) and Cd(II) ions using a bentonite clay in the homoionic potassic form. The pretreated clay was characterized through N₂ adsorption, X-Ray diffraccion (DRX) and Zero Point Charge (ZPC), which indicated a mesoporous materials with typical plane interlayer distances. The lead and cadmium removal followed a pseudo-second order, according to the chemical reaction kinetic model, which may be related to the chemisorption process as rate-limiting step. Isotherms showed a favorable behavior mainly for lead removal even in competitive solutions due to its high electronegativity. Thermodynamic parameters showed that the clay affinity sequence is $Pb^{2+} > Cd^{2+}$.

1. Introduction

Bentonite clay is a 2:1 mineral with one octahedral sheet and two silica sheets, which forms a layer. It carries a net negative charge due to the broken bonds around the edges of the silica–alumina units. This would give rise to unsatisfied charges, which would be balanced by the exchanging cations (Bhattacharyya and Gupta, 2008). Therefore, bentonite clay has been studied as ion exchanger and/or adsorbent due to its framework (Sajidu et al., 2008). It is noteworthy that the bentonite clay can change its removal mechanism according to its pretreatment. It can be only calcined in order to increase the mechanical resistance and to eliminate some impurities (Vieira et al., 2010). Moreover, it can be submitted to an ion exchange process to become homoionic, with an increased sorption capacity (Ayari et al., 2007). Studies with homoionic clays are scant. In order to fulfill this lack of information this paper aimed to investigate bentonite clay treated with potassium. Then, the main objective of this paper was to investigate the potassic bentonite as a sorbent of Cd(II) and Pb(II) ions. It was investigated the kinetics and equilibrium data for single (Pb(II) or Cd(II)) and equilibrium data for competing (Pb(II)-Cd(II)) systems at 25, 30 and 40 °C.

2. Experimental

2.1 Clay

A bentonite clay sample from the city of Boa Vista-PB, located in the northeastern of Brazil, was used as sorbent. The clay was firstly screened ($d_p = 0.064$ mm) and calcined at 500 °C for 24 h. Then, the sample was submitted to the potassium treatment. Calcined clay was put in contact with KCl (0.25 mol/L) in a ratio 25 g solid /105 mL solution de

KCl. The system was stirred for 4 h and exhaustively washed with distilled water to eliminate, from the solid phase, not retained K^+ ions. Sample was characterized by N_2 adsorption, DRX and pH_{ZPC} (zero point charge).

2.2 Cadmium and Lead solutions

The initial concentration of 1.5 meq/L of each cation was obtained from the respective reagent grade salt in the chloride form. All aqueous solutions were analyzed through the atomic absorption spectrophotometry in a Varian 50B equipment. The speciation curve of the ions in aqueous solution at a concentration of 1.5 meq/L for Pb(II) and Cd(II) was determined through the HYDRA® software.

2.3 Kinetic studies

The adsorption experiments were carried out using a 1.5 meq/L solution of lead or cadmium. 20 mL of each solution were added in a glass flask with 0.2 g of the pretreated clay. Flasks were put in a shaker at a constant stirring. Temperature and pH were kept constant at 25 °C and 4.0, respectively. The kinetic experimental data was obtained when each flask was removed from the shaker at different contact times (0-150 min), the solution was filtered and the cations in the aqueous phases analyzed. The amount of cation removed (q_t) was obtained through a mass balance. Lagergren equation was adjusted to experimental data (Ho, 2004). It is a pseudo-first order kinetics (Ricordel et al., 2001). Pseudo-second order model was based on the sorption capacity of the solid phase (Febrianto et al., 2009).

2.4 Equilibrium studies

The isotherms were constructed taking into account the equilibrium time obtained by the kinetic data. Experiments of single sorption were based on Barros et al. (2003). They were carried out adding 0.2 g of pretreated clay in 20 mL of metal solution with different initial concentrations (1-5 meq/L). pH values were corrected to 4. The single equilibrium data was fit to Langmuir and Freundlich models. Competitive solutions were carried out using different equivalent ratios (0.1 – 0.9) of each cation in a total concentration of 3 meq/L.

2.5 Thermodynamic studies

The thermodynamic parameters for the adsorption process: sorption enthalpy (ΔH), sorption free energy (ΔG) and sorption entropy (ΔS) were estimated according to Vieira et al. (2010).

3. Results and discussion

The pre-treated clay presented a BET superficial area as 120 m^2/g and average pore size of 42 Å for K-bentonite. The XRD analysis for K-bentonite showed quite similar results to those published in Vieira et al. (2010). The K-bentonite sample has a basal spacing of 4.45 Å, which is considered a narrow space for ion exchange processes. pH_{ZPC} value obtained for the K-bentonite clays is 5.6. Thus, in order to ensure that the clay surface has a positive charge to promote the exchanging reactions the sorbent was put in contact with solutions with $pH < pH_{ZPC}$, that is $pH = 4$. Moreover, at such pH, results from the Hydra® software showed that Pb(II) solutions present relevant amount of Pb(II) species

and small quantities of the complexes PbOH^+ and $\text{Pb}(\text{OH})^{+3}$. On the other hand, Cd(II) speciation showed that the specie Cd(II) is the most pronounced one, with negligible amount of complexes. Such differences as well as the nature of the cation may influence in the ion removal.

Figure 1 shows the kinetic results for both ions in single ion exchange. One may observe that there are slightly differences between both models tested herein.

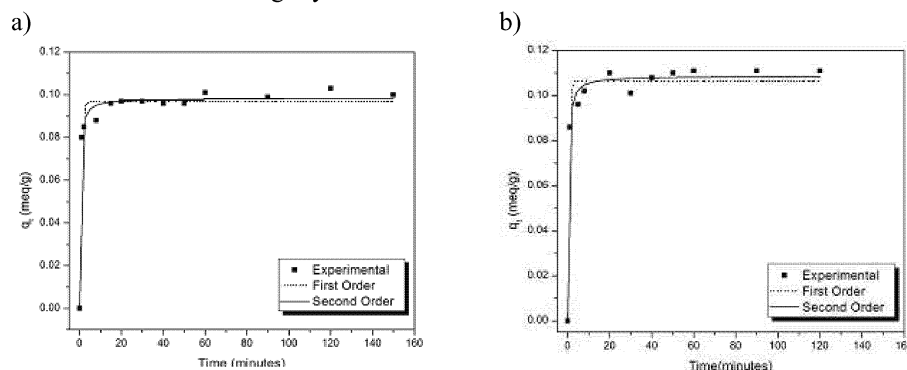


Figure 1: Kinetic experimental data and mathematical models. a) Lead, b) Cadmium

The numerical data is presented in Table 1. According to the correlation factor it is possible to assure that the pseudo-second order model better fits the experimental results. This could be related to the ion sorption in the basal spaces of the clay structure.

Table 1. Pb(II) and Cd(II) adsorption rate coefficients for pseudo-first-order and second-order models on K-bentonite clay.

Ion	Kinetic model	K*	q_{eq} (meq/g)	R ²
Pb(II)	Pseudo-1 st order	1.011±0.183	0.097±0.001	0.977
	Pseudo-2 nd order	24.17±5.17	0.099±0.001	0.990
Cd(II)	Pseudo-1 st order	0.531±0.082	0.106±0.002	0.963
	Pseudo-2 nd order	9.021±1.551	0.110±0.002	0.984

*K = min⁻¹ for the pseudo first order and g/meq.min for the pseudo second order.

The equilibrium data is presented in Figure 2. It is observed a favorable behavior of lead sorption in the temperatures here investigated. It seems that a more pronounced plateau is related to the isotherm at 25 °C while increasing temperatures promoted a tendency to a smoother curvature. This may be related to formation of multilayer sorption. The Langmuir model best fit the equilibrium data. Quantitative results will be discussed in Table 2.

Cd(II) isotherms can be seen in Figure 3. It is noteworthy that, although having the same charges, the sorption behavior of cadmium ions is totally different. Cadmium isotherms present a favorable shape (McCabe et al., 2001) typical of favorable multilayer sorption processes. This is due to the ion characteristics. Cadmium is less electronegative than lead and, as a consequence, less attracted to the chemisorption sites. However, the potassic bentonite retains, experimentally, up to 0.55 meq Cd(II)/g

at 25 °C and removes almost 0.17 meq/g of lead. Cadmium ion is better retained, although with weaker attraction, due to its smaller ionic radius. It can be better accommodated in the basal space of the bentonite clay. Considering lead ions, at pH = 4, there are also some other species besides Pb(II) that may inhibit an easy accommodation of such ions in the basal space.

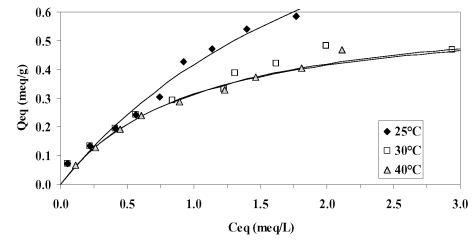
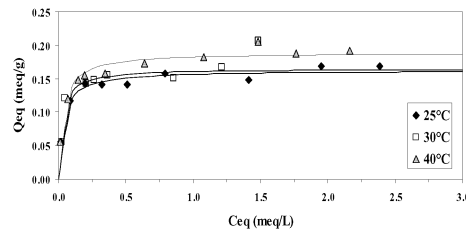


Figure 2: Equilibrium data for single lead sorption and the best isotherm model

Figure 3: Equilibrium data for single cadmium sorption and the best isotherm model

The competitive isotherms can be seen in Figure 4. In all cases lead ions are more sorbed than cadmium ions. Probably the electrical double layer is formed. Lead ions form the first layer, then, after accommodation of the chloride anions, the less electronegative cadmium ions are accommodated.

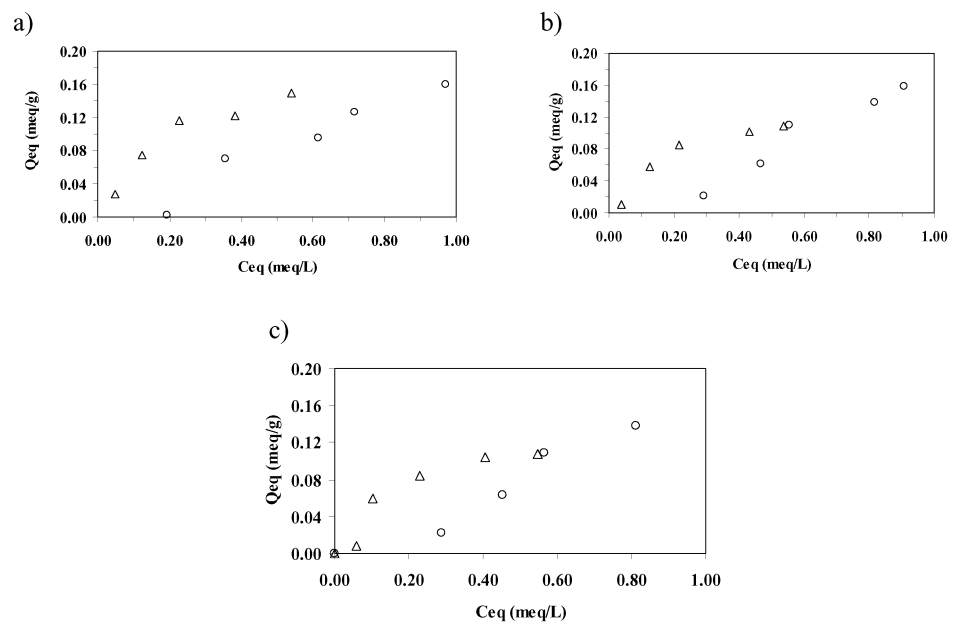


Figure 4: Competitive equilibrium data at a) 25 °C, b) 30 °C and 40 °C. Δ Pb(II); \circ Cd(II).

The parameters of the single equilibrium data are shown in Table 2. Unfortunately the competing experimental data was not enough to estimate parameters of isotherm models. In both single systems, Langmuir model seems to be the one the best represents the experimental data. In the investigated concentration range it was observed that Langmuir model could estimate q_{\max} close to the experimental data for lead ions. 0, such phenomenon was not observed in the Cd(II) equilibrium data as q_{\max} is far from the experimental data mainly at 25 °C. Probably, this investigate range may be the beginning of the cadmium isotherm. Then, $q_{\max} = 1.543$ meq/g for Cd(II) ions should be considered as a preliminary result.

Table 2. *Parameters of the isotherm models*

	Langmuir			Freundlich			
	T °C	q_{\max}	b	R ²	a	1/n	R ²
Pb ²⁺	25	0.162 ±0.04	27.59 ±4.40	0.984	0.154 ±0.006	0.147 ±0.031	0.808
	30	0.165 ±0.006	34.85 ±7.79	0.973	0.170 ±0.013	0.166 ±0.049	0.742
	40	0.189 ±0.007	26.63 ±5.86	0.975	0.191 ±0.008	0.190 ±0.028	0.910
Cd ²⁺	25	1.534 ±0.417	0.361 ±0.139	0.972	0.399 ±0.012	0.735 ±0.064	0.975
	30	0.630 ±0.018	0.998 ±0.059	0.979	0.316 ±0.010	0.465 ±0.043	0.970
	40	0.614 ±0.034	1.040 ±0.149	0.986	0.293 ±0.012	0.471 ±0.050	0.959

The thermodynamic data is presented in Table 3. Based on the sorption approach it is possible to note that lead and cadmium sorption is favorable ($\Delta G < 0$). From a consideration of ΔG values the affinity sequence is $\text{Pb}^{2+} > \text{Cd}^{2+}$ for the temperature range investigated. Both entropy changes are negative. For a closed but not isolated system, as the flasks where the experimental points were obtained, the entropy may decrease since the surroundings have a gain in this property. Therefore, $\Delta S < 0$ is possible to occur and was already reported (Barros et al., 2004). The enthalpy changes are negative indicating an exothermic process.

4. Conclusions

With results presented herein it is possible to conclude that the bentonite clay treated with potassium may remove lead and cadmium. Moreover, sorption kinetics follows a pseudo-second order model. The isotherms provided a favorable behavior and, due to the higher electronegativity, lead seems to be better attracted, and a higher amount of ions is removed. Increasing temperatures decreased Cd(II) removal, probably due to the weaker multilayer sorption. The affinity sequence is $\text{Cd}^{2+} > \text{Pb}^{2+}$. The entropy and

enthalpy are negative, which means an increase in the system order and an exothermic process. The bicomponent isotherms provided a higher affinity to lead ions instead of cadmium ones.

Table 3. *Thermodynamic parameters of adsorption*

	T°C	ΔG (J/mol)	ΔS (J/molK)	ΔH (J/mol)
Pb ²⁺	25	-3148		
	30	-2644	-20.56	-9140
	40	-2644		
Cd ²⁺	25	-881.1		
	30	-695.4	-137.41	-42049
	40	1036.6		

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