COMPARATIVE THERMODYNAMIC STUDIES OF AMMONIUM ION ADSORPTION ONTO Na-CLINOPTILOLITE

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ABSTRACT: In the present study, the adsorption thermodynamic behavior of ammonium ion onto a Na-clinoptilolite zeolite was evaluated. Equilibrium data (isotherms) were obtained at temperatures of 25, 35 and 45°C and were used in the estimative of thermodynamic parameters. Methodologies extensively applied to calculate equilibrium constant (K_0) were used on the estimative of change in free energy ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$). Depending on the methodology, the process was characterized as exothermic or even endothermic, proving the poor correlation between the methodologies to estimate such important data. The method utilized by Gaines and Thomas to estimate K_0 was recognized as the most correlated to the equilibrium data. The Langmuir, Freundlich and Redlich-Peterson models were adjusted to data and both Freundlich and Redlich-Peterson were found as the best fitting models, suggesting the occurrence of a reversible and energetically heterogeneous adsorption process.

KEYWORDS: adsorption; thermodynamic, zeolite; ammonium ion.

1. INTRODUCTION

Wastewater from petrochemical, pulp and paper mill industries, agricultural production and the nutrient loss from soil to water as a result of manure disposal have been associated as possible sources of nitrogen high levels found in surface and ground waters (Afonso et al., 2008; Ugurlu and Karaoglu, 2011; Saltali et al., 2007). Nitrogen in the form of ammonium ion (NH_4^+) or dissolved ammonia (NH_3) is one of the main forms of nitrogen present in these effluents and can cause serious environmental impacts if released into water bodies without proper treatment. Ammonia nitrogen contributes to eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity (Marañón et al., 2006).

Some of wastewater treatments that performs the removal of ammonia nitrogen are biological treatment, air stripping, reverse osmosis, ion exchange and distillation (Metcalf & Eddy, 2003). Among these, the ion exchange figures as an attractive alternative since it does not consume significantly amounts of energy and can be applied in the presence of high BOD and anions as phosphate or sulfate, constituents frequently present on effluents (Moussavi et al., 2011; Huang et al., 2010).

Zeolites are inorganic materials capable of accomplish ion exchange and with high affinity to ammonium ion. Despite the great interest in adsorption with zeolites, few data exist referred to the thermodynamic and the estimative proceedings of equilibrium constant (K_0) of adsorption by mechanism of ion exchange.

The objective of this study was to estimate the equilibrium constant (K_0) for ammonium adsorption onto a Na-clinoptilolite using the most extensively used methodologies and demonstrate how the thermodynamics assumptions of each one can affect the conclusions about the energy involved in the sorption process. Also, we point out the most reasonable method to obtain K_0.

2. MATERIALS AND METHODS

2.1. Materials

The Na-clinoptilolite (CS) used in this study was supplied from Celta Brazil Company, São

Paulo, Brazil, with a particle size of 0.4-1.0 mm. The CS as received was sieved to remove powder, present in a large quantity on commercial product, and to select a shorter range of size (0.7-1.0 mm) prior to use in the experiments.

Analytical grade ammonium sulfate $(NH_4^+)_2SO_4$ and deionized water were used in the preparation of the stock NH_4^+ solutions. Chloride acid solution was used for the pH control during the adsorption experiments. A membrane of 0.45 µm nominal pore size was used for collecting the suspension to NH_4^+ analysis after adsorption.

2.2. Batch Experiments

The equilibrium experiments were performed in a thermostatic shaker bath in the concentration range of 50-1,200 mg.L^{-1} of ammonium, contact time of 3h and zeolite dosage of 12.5 g.L^{-1}. The sorption isotherms were obtained at temperatures 25, 35, and 45°C. The suspension was collected and an ultraviolet spectrophotometer (UV1600, Pró-Análise) was used to determine the residual concentration of ammonium (APHA et al., 1992). In this paper, the term ammonium is used in reference to the sum of NH_3 and NH_4^+ species simultaneously present in the solution.

The adsorption capacity at equilibrium, expressed as q_e (mg.g^{-1}) was determined by Equation 1:

$$q_e = \frac{V(C_0 - C_e)}{m} \qquad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of ammonium in solution (mg.L^{-1}), respectively. V is the solution volume (L) and m is the mass of adsorbate (g).

2.3. Non-linear Optimization

Langmuir (Equation 2), Freundlich (Equation 3) and Redlich-Peterson (Equation 4) models were evaluated in the representation of experimental data.

$$q_e = \frac{q_m.K_L.C_e}{1 + K_L.C_e} \qquad (2)$$

$$q_e = K_F.(C_e)^{1/n} \qquad (3)$$

$$q_e = \frac{q_{RP}.C_e}{1 + K_{RP}.C_e^{\beta}} \qquad (4)$$

where q_m is the maximum adsorption capacity at equilibrium (mg.g^{-1}), K_L is the Langmuir constant (L.mg^{-1}) related to adsorption energy, K_F (mg.g^{-1})(L.mg^{-1})$^{1/n}$ is related to adsorption capacity, n (dimensionless) is an empirical constant related to heterogeneity on energy adsorption, q_{RP} (L.g^{-1}), K_{RP} (L^{β}.$mg^{-\beta}$) and β (dimensionless) are Redlich-Peterson constants.

The model's parameters were assessed by non-linear regression using the Origin 8.5 software (OriginLab Corporation, Northampton, Mssachusetts, EUA) and reducing the value of the objective function (F_{obj}) of the minimum-squares, as represented in Equation 5.

$$F_{obj}(\phi) = \sum_{i=1}^{s} (q_{e,mod}^{i} - q_{e,exp}^{i})^2 \qquad (5)$$

where $q_{e,mod}$ and $q_{e,exp}$ are the dependent variable estimated by the model and obtained experimentaly, respectivetly. The above-written i indicates the considered data and s is the total experimental data.

The accuracy of the models to the experimental data was examined by Corrected Akaike's Information Criterion (*AICc*), represented in the Equation 6:

$$AIC_C = -s.\ln\left(\frac{SSE}{s}\right) + 2.k + \left[\frac{2.k(k+1)}{s-k-1}\right] \qquad (6)$$

where s, SSE and k represents the total number of experimental data, sum of square of errors and the models parameters number, respectively (El-Khaiary et al., 2011).

3. THERMODYNAMIC ANALYSIS

The chemical reaction equilibrium constant (K_0) provides the feasibility (tendency to the formation of products or reactants) and extension of a given reaction (Skoog et al., 2006). The change in free energy ($\triangle G$) quantifies the energy involved in the adsorption and so it is possible to characterize the adsorption as physical or chemical with respect to strength of energy. The enthalpy ($\triangle H$) characterizes the phenomenon as exothermic

or endothermic, while the entropy $(\triangle S)$ gives us an idea about the degree of disorder of the system.

3.1. Equilibrium Constant

Considering the reaction of ammonium adsorption through ion exchange with Na-clinoptilolite:

$$NH_{4(l)}^{+} + ZNa_{(s)}^{+} \rightleftharpoons ZNH_{4(s)}^{+} + Na_{(l)}^{+} \quad (7)$$
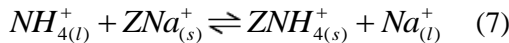
The expression for K_0 is then represented as follows (Skoog et al., 2006; Perry and Green, 2008):

$$K_0 = \frac{[\gamma_{ZNH_4^+}.ZNH_4^+].[\gamma_{Na^+}.Na^+]}{[\gamma_{NH_4^+}.NH_4^+].[\gamma_{ZNa^+}.ZNa^+]} \quad (8)$$

where NH_4^+, ZNa^+, ZNH_4^+ and Na^+ are the species involved in the reaction; γ_{ZNH4+}, γ_{NH4+}, γ_{Na+} and γ_{ZNa+} are the activity coefficients.

Because sodium and ammonium ions have same charges, the stoichiometric coefficients are all equal to unity and consequently the thermodynamic parameter K_0 will be dimensionless in the case of ion exchange of ammonium ion onto Na-clinoptilolite.

The quantification of concentrations in case of adsorption is complicated because the species varies between fluid (l) and adsorbed phase (s), as shown in Expression 7. Due to the difficulty in quantifying the concentrations of adsorbed species and the activity coefficients, the estimative of K_0 have been done under different approaches. The most frequently used methodologies in the parameter estimative are shown as follows.

__3.1.1. Thermodynamic analysis of Gaines and Thomas (G&T):__ Gaines and Thomas (1953) proposed a methodology for calculating K_0 firstly developed to ion exchange adsorption on clay minerals. The development of equation parts from the expression for the equilibrium constant K_0 as shown in Equation 8. In the sequence, the authors use a thermodynamic analysis of the chemical equilibrium theory formulated by Gibbs and the equation of Gibbs-Duhem to solid phase, resulting in the following expression for the calculation of K_0:

$$\ln K_0 = (Z_B - Z_A) + \int_0^1 \ln K_C.dA_Z \quad (9)$$

where Z_A and Z_B are the charges of the ions involved in process, A_Z represents the equilibrium concentration to initial concentration ratio (C_A/C_0) and K_C is the Kielland coefficient, given by:

$$K_C = \frac{A_Z(1 - A_S)}{(1 - A_Z)A_S} \quad (10)$$

where A_S represents the adsorption capacity at equilibrium to maximum adsorption capacity ratio $(q_e/q_{emáx})$.

How Z_A and Z_B are the same for the case of ammonium and sodium ions, Equation 9 results:

$$\ln K_0 = \int_0^1 \ln K_C.dA_Z \quad (11)$$

Therefore, to estimate K_0, it is necessary to integrate the area below the curve obtained from plotting $ln K_C$ versus A_z.

__3.1.2. Thermodynamic analysis of Biggar and Cheung (B&C):__ According to Biggar and Cheung (1973) the concentration of the adsorbed compound at equilibrium (C_C) is expressed in mass of adsorbate per volume of solvent *in contact with the surface of the adsorbent* $(\mu g.mL^{-1})$. In addition, the authors considered just one specie involved on adsorption, resulting:

$$K_0 = \frac{\gamma_C}{\gamma_A}.\frac{C_C}{C_A} \quad (12)$$

To quantify C_C in the required unity, the authors propose the following calculus:

$$C_C = \frac{S.N.D.q_e}{P.A} \quad (13)$$

where S is the cross section of the solvent $(cm^2.molecule^{-1})$ molecule; N is Avogadro number $(molecule.mol^{-1})$; D is the density of water; q_e is the adsorbed amount of solute in the sorbent; P is the molecular weight of water and A is the specific surface area of the sorbent $(cm^2.g^{-1}$ zeolite).

After estimating C_C for each equilibrium point $(q_e; C_A)$ the authors apply a graphical extrapolation of the curve constructed by (C_C/C_A) versus C_A to zero C_A, as represented by the expression:

$$lim_{C_A \to 0} \frac{C_C}{C_A} = K_0 \tag{14}$$

Through this approach, the activity coefficient (γ) is considered equal to unity (1), since the system is in the condition of infinite dilution. In the original text (1973) the extrapolation to infinite dilution ($C_A \to 0$) is described as it is shown in Equation 14 however, on the published work it is represented as $C_C \to 0$. This fact may have originated the different interpretations found in publications in the adsorption area.

3.1.3. Thermodynamic analysis of Khan and Singh (K&S):
Khan and Singh (1987) applied the graphical extrapolation proposed by Biggar and Cheung, except that they do for the curve constructed by (C_C/C_A) versus C_C, extrapolating to zero C_C. Additionally, the authors consider C_C as equal to q_e (mmol.g^{-1}), and doing this, K_0 reveals to have a dimension of mL.g^{-1}. This methodology can be expressed as:

$$lim_{C_C \to 0} \frac{C_C}{C_A} = K_0 \tag{15}$$

The authors do not justify the approaching made to the estimative of K_0 neither the fact of assigning a dimension to the parameter. Nevertheless, this methodology can be found in a wide number of publications in the field of adsorption (Raji et al., 1998; Lyubchik et al., 2004; Schneider et al., 2007; Piccin et al., 2011).

3.1.4. Thermodynamic analysis from Langmuir coefficient ($K_0 \sim K_L$):
The chemical reaction equilibrium constant K_0 is frequently estimated based on the Langmuir constant K_L. By this method, K_L is generally converted to dimension of solution volume per quantity (molar or mass) of adsorbate, in L.g^{-1} or L.mol^{-1}.

This method extensively used by researchers in adsorption, has been applied to a wide range of concentrations. Despite the widespread use, there is no mention concerning about the condition of infinite dilution or the activity coefficients.

3.1.5. Thermodynamic analysis considering species in the aqueous phase:
Some authors (Ugurlu and Karaoglu, 2011; Zheng et al., 2008) estimate the concentration of the adsorbed compound (C_C) by the difference of

initial and equilibrium concentrations of solute in the aqueous phase, resulting:

$$K_0 = \frac{\gamma_C}{\gamma_A} \cdot \frac{C_C}{C_A} = \frac{C_{A0} - C_A}{C_A} \tag{16}$$

The contribution of activity coefficients (γ) is apparently not considered. Zheng et al. (2008) applied Equation 16 at ammonium initial concentration (C_{A0}) of 80 mg.L^{-1}, but in the published work it was not possible to find the explanation why the authors have chosen the value.

3.1.6. Thermodynamic analysis proposed in this work:
It is suggested to do the calculation as expressed in Equation 16 for each equilibrium point and after would be appropriated to include an extrapolation of the values to the infinite dilution condition, as proposed by Biggar and Cheung (B&C).

3.2. Thermodynamic Parameters ΔG, ΔH and ΔS

The thermodynamic parameters such as change in free energy ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$) are estimated using the Equations 17 and 18:
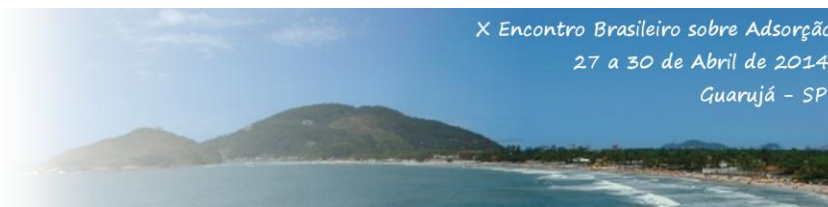
$$\Delta G = -R \cdot T \cdot ln\, K_0 \tag{17}$$

$$ln\, K_0 = \frac{\Delta S}{R} - \frac{\Delta H}{R.T} \tag{18}$$

where R is the universal gas constant (8.314 J.mol^{-1}.K^{-1}) and T is the temperature in Kelvin (K).

From the Equation 17 it can be observed that K_0 must be dimensionless, once the multiplication of R and T results on the $\triangle G$ unit (kJ.mol^{-1}).

To evaluate the strength of the energy involved on adsorption, the measure of the free energy must be related to the condensation energy of the adsorbate molecule (Adamson, 1982). That is, if the free energy of the system is significantly greater than the energy of condensation, it must be considered the occurrence of chemisorption and if it is close to or less than the energy of condensation it must be considered the occurrence of physisorption. The energy of condensation of NH$_3$ is 20 kJ.mol^{-1} to temperature of 20°C and 18 kJ.mol^{-1} to 40°C (Perry and Green, 2008).

4. RESULTS AND DISCUSSION

4.1. Isotherms

Figure 1 shows the graphical representation of ammonium adsorption onto Na-clinoptilolite obtained from batch studies at 25, 35 and 45°C.
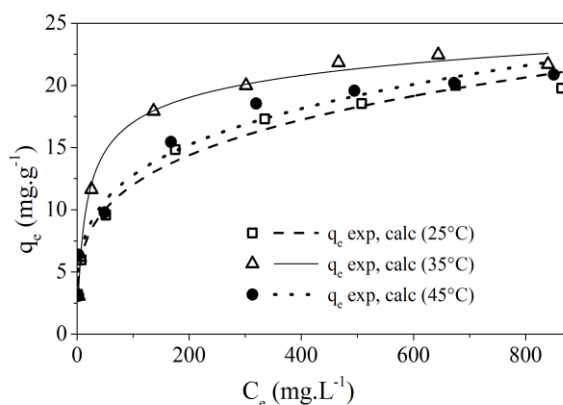

Figure 1. Ammonium adsorption isotherms at 25, 35 and 45°C and graphical representation of models who showed the best fitting (contact time 3 h; zeolite dosage 12.5 g.L^{-1}; pH 5.5±1.0).

Observing the sorption capacity (q_e) achieved for the equilibrium concentration (C_e) of 800 mg.L^{-1}, with values of 19.8, 21.7 and 20.9 mg.g^{-1} (with 0.8 of standard deviations) at 25, 35 and 45°C respectively, it can be seen that the capacity of the adsorptive material does not change significantly with increasing temperature. Despite from the very closely values, it can be seen that they were highest for temperature of 35°C and lowest for 25°C. That is, there is an increase in q_e with increasing temperature from 25 to 35°C and subsequent decrease in q_e with increasing temperature from 35 to 45°C. Apparently, the improvement in adsorption capacity has a limit, and so does not change regularly.

This same behavior was observed by Zheng et al. (2008), studying the removal of ammonium by zeolite containing potassium as exchangeable cation. It was observed that the removal efficiency showed an increase with increase in the temperature from 20 to 30°C and decreased with increasing temperature of 30 to 40°C and then continued to drop to 50°C.

Table 1 presents the results from non-linear optimization of the Langmuir, Freundlich and Redlich-Peterson models to experimental data.

Data of ammonium equilibrium adsorption at temperatures of 25, 35 and 45°C were best correlated to Freundlich, Redlich-Peterson and Freundlich, respectively, as shown by the solid and dashed lines in Figure 1.

Table 1. Statistical parameter *AICc* and constants from Langmuir, Freundlich and Redlich-Peterson models fitted to experimental data.

Parameter/Isotherm	25°C	35°C	45°C
Langmuir			
K_L (L.mg^{-1})	0.0219	0.0495	0.020
q_m (mg.g^{-1})	20.240	22.075	21.446
AICc	13.995	5.657	18.184
Freundlich			
K_F (L$^{1/n}$. g^{-1}. mg$^{(n-1)/n}$)	3.622	4.778	4.004
n	3.841	4.157	3.966
AICc	1.081	15.648	8.799
Redlich-Peterson			
K_{RP} (L$^{\beta}$.mg$^{-\beta}$)	1.434	0.132	1.759
β	0.769	0.911	0.775
q_{RP} (L.g^{-1})	6.273	1.665	8.381
AICc	4.077	2.863	13.747

Freundlich isotherm fits better to reversible and heterogeneous systems in accordance with materials such as zeolites, which can be easily regenerated. Furthermore, the zeolite used in this study consists of clinoptilolite, which have pores of different and specific sizes, therefore, a material with heterogeneous surface.

4.2. Thermodynamic Parameters

Figure 2 shows the application of the methods for estimative of K_0 previously cited, except for the one who utilizes Equation 16 and the one based on the K_L coefficient, once that graphical extrapolation is not necessary in both methods.

The method proposed by G&T was applied. The values of $ln\ K_C$ were plotted as function of A_z, as can be seen in the Figure 2.a. The integration of

curves obtained at each temperature was estimated and corresponds to *ln* K_0. Applying the exponential, K_0 was finally obtained.

Figure 2.b shows the application of the methodology proposed by B&C. The resulting values from Equation 13 were converted to C_C/C_A, and plotted as function of ammonium equilibrium concentration (C_A). The exponential trend lines represent the extrapolation of data to the infinite diluted condition, for each temperature evaluated. The linear coefficients correspond to K_0 values.

The application of K&S method is shown in Figure 2.c. The values of C_C/C_A were plotted as function of compound concentration at equilibrium (C_C) and an exponential trend line was added. Through the graphical extrapolation to zero C_C the values of K_0 were then obtained.

In the Figure 2.d it is shown the application of methodology proposed in the present study. The resulted values of Equation 16 (C_0-C_A/C_A) are plotted as function of equilibrium concentration (C_A) for each equilibrium point in the evaluated temperatures. After, it was applied the graphical extrapolation to zero C_A, characterizing an infinite dilution condition.

Table 2 shows the results from application of all methodologies above mentioned, except the method which utilizes Equation 16 for the arbitrary value of 80 mg.L^{-1}. As can be seen, the values of K_0 showed differences in the order of 10^5, depending on the methodology used.

The values of K_0 obtained from the methodology proposed by G&T, K&S and from this study are very close to those found in the literature. Alshameri et al. (2013) obtained values of 2.89, 2.01 and 0.82 in a study using sodium natural zeolite at temperatures of 25, 35 and 45°C. Using the method by G&T in experiments with clinoptilolite zeolite in the sodium form, Wang et al. (2008) obtained values of 3.7, 3.0 and 2.1. Zheng et al. (2008) found values of 7.82, 5.65 and 4.00, at temperatures of 30, 40 and 50°C using a synthesized zeolite.

The method proposed by G&T is the only one where values of K_0 agree to what was observed in the isotherms: the highest value obtained for 35°C and the lowest for 25°C. Both methods from B&C and from the present study had values that increased proportionally with temperature. Considering the method that K_0 is proportional to K_L, the resulting values reflect a different behavior, with the following order of K_0: 45°C < 25°C < 35°C.
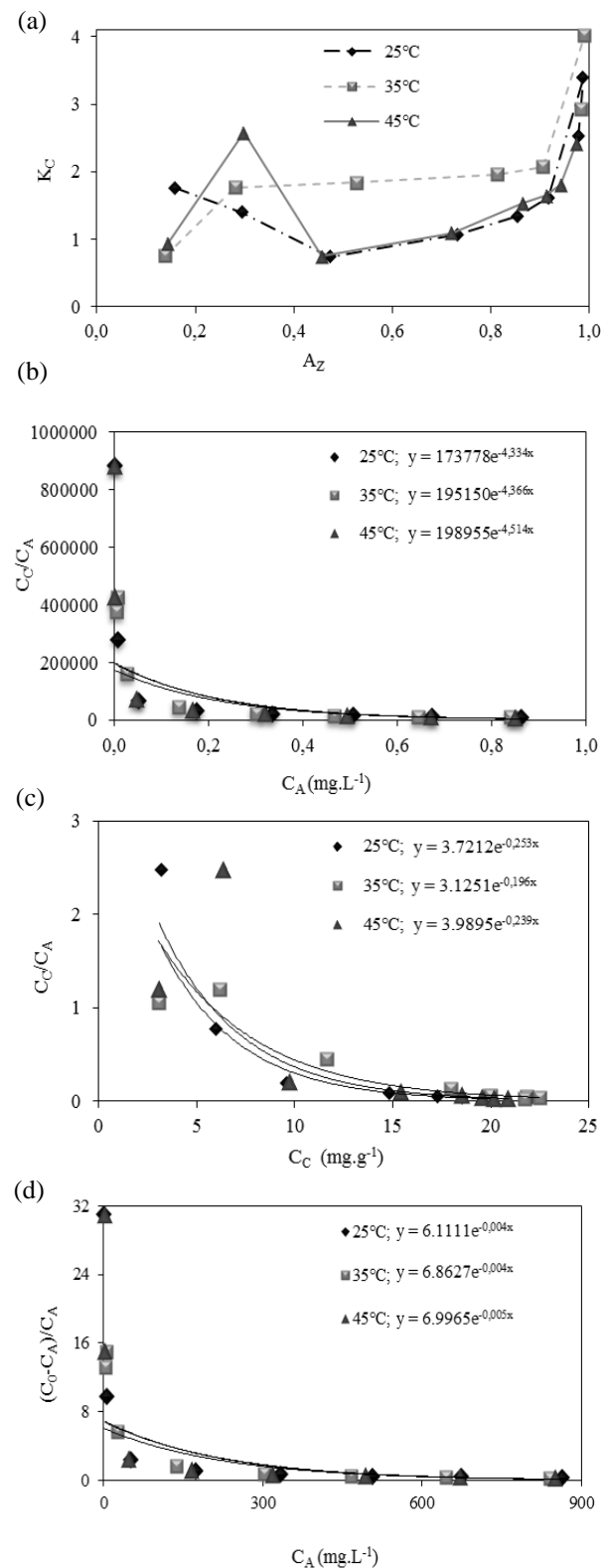

Figure 2. Application of methodology for the estimative of K_0 applied by (a) Gaines and Thomas, (b) Biggar and Cheung, (c) Khan and Singh and (d) proposed in this study.
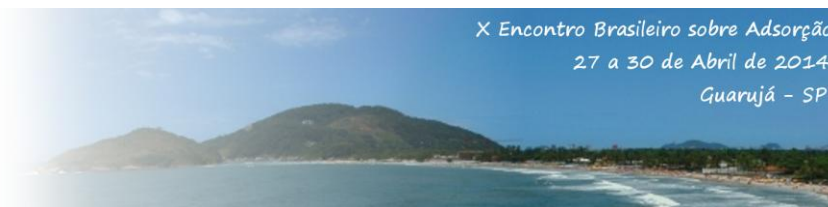
Table 2. Equilibrium constants (K_0).

Method	Unit	Temperature		
		25°C	35°C	45°C
(G&T)	*	2.81	4.98	3.11
(B&C)	*	1.74×10^5	1.95×10^5	1.99×10^5
(K&S)	(L.g^{-1})	3.721	3.125	3.989
K_L	(L.g^{-1})	21.855	49.547	20.068
Present study	*	6.11	6.86	7.00

*dimensionless

The change in Gibbs free energy ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$) estimated for each methodology are shown in Table 3.

Table 3. Thermodynamic parameters.

Method	$\triangle G$*			$\triangle H$*	$\triangle S$**
	25°C	35°C	45°C		
(G&T)	-2.56	-4.11	-3.00	4.5	25
(B&C)	-29.91	-31.21	-32.27	5.4	118
(K&S)	-20.38	-20.62	-21.93	2.6	76.4
K_L	-14.82	-17.41	-15.58	-2.6	43
Present study	-4.49	-4.94	-5.15	5.4	33

*kJ.mol^{-1}
**J.mol^{-1}K^{-1}

The $\triangle H$ value from the B&C method and the one proposed in this study were the same (5.4 kJ.mol^{-1}), suggesting an endothermic system.

An important aspect about $\triangle H$ value is that the G&T method resulted in K_0 values that agreed with equilibrium behavior and additionally, the $\triangle H$ was very close to methods from B&C and from the present study. From this observation, it was concluded that G&T method was the most reasonable in obtaining the equilibrium constant. In addition, it was noted that both the $\triangle G$ value

and $\triangle S$ found by the application of G&T methodology are very close to that found from method proposed in this study. Both methods characterize the adsorption mechanism in terms of energy involved, as physisorption, which is in agreement of ion exchange processes, that can be easily regenerated. Due to this proximity of values obtained and to the fact that both methods characterizes the system as endothermic and with occurrence of physisorption, and additionally, because the $\triangle H$ value was the same as found from the B&C method, we suggest that the methodology here proposed is a plausible and facile alternative in the estimative of thermodynamic parameters.

The method that estimates K_0 from K_L was the only one that indicated an exothermic system, since the value of $\triangle H$ is negative. This behavior is very unlike to observations taken from others methodologies. Thus, it could be said that the method of estimating K_0 from K_L should be reviewed, especially regarding its application in adsorption by ion exchange.

All methods yielded positive entropy values indicating an increase in the degree of disorder of the system.

Given the observations, it is concluded that the system of ammonium ion adsorption by sodium zeolite is endothermic and with entropy increase. $\triangle G$ values suggest that the process is spontaneous and mainly governed by physisorption.

5. CONCLUSIONS

From the isotherms, it can be concluded that the sorption equilibrium behavior of ammonium onto sodium zeolite is best fitted to Freundlich model for 25°C and 45°C and Redlich-Peterson to 35°C, indicating a reversible process and material with energetically heterogeneous surface.

Based on the findings from thermodynamics studies, it was verified that depending on the methodology considered in the calculation of K_0, a difference in the order of 10^5 can be obtained. The thermodynamic parameters $\triangle G$ (lower than the energy of condensation of NH_3) and $\triangle H$ (positive) characterizes the removal of ammonium by sodium zeolite as physisorption and endothermic in nature. The $\triangle S$ reveals an increase of entropy of the system. It was observed that the equation developed by Gaines and Thomas to estimate K_0 was the most correlated to the equilibrium data. Also, it can be concluded that from the method
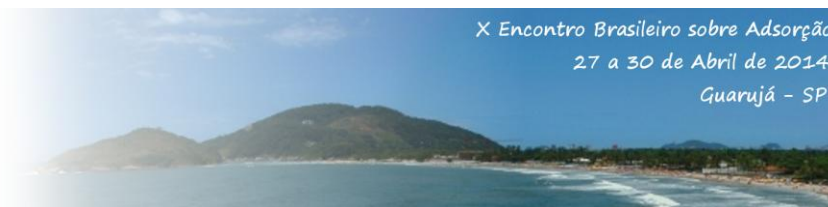
proposed in this study to estimate K_0, we were able to estimate $\triangle G$, $\triangle H$ and $\triangle S$ parameters with values that were very close to the ones obtained from Gaines and Thomas methodology and with the advantageous of applying a simpler calculus.

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