Nitrate Adsorption using Sugar Cane Bagasse Physicochemically Changed

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Abstract

For avoiding the possible environmental impacts the adequate treatment is necessary, being one of the alternatives the adsorption process. Studies involving kinetics, equilibrium and thermodynamic were performed for adsorption of nitrate in adsorbent materials modified chemically and physically. The adsorbents were obtained by physical-chemical modifications with heating of sugar cane bagasse and addiction of phosphoric acid 3 mol L^{-1} with temperatures ranging until 480ºC in oven. With the obtained results for kinects of adsorption it was found a max adsorbed quantity in thirty minutes. The equilibrium study demonstrate higher removal percentages of nitrate in lower initial concentrations, and the thermodynamic studies demonstrate better results for adsorption at 25ºC. The occurrence of multilayers was also observed according to Freundlich model, and with predominance of non-spontaneous system of adsorption. Among the positive aspects of this study is the possibility of the use of an agro industrial waste, generated in large quantities in the country and still with few use, and that the adsorption process of contaminant removal is economically viable, being interesting the development and improve of this process, searching for higher efficiency of the process.

Keywords: Isotherm, adsorption kinetics, thermodynamic of adsorption

Introduction

The nitrate ion is a naturally present in natural waters ion derived from the decomposition of organic matter, igneous rocks and drainage areas. However, some factors may contribute to the increase of their concentration, such as industrial and domestic sewage discharges and the use of fertilizers containing inorganic nitrate (PÁDUA; FERREIRA, 2006). When found excessively in water bodies it can cause eutrophication, because it is a limiting agent to growth of plant biomass, causing serious state of deterioration (MANAHAN, 2013), especially for any mortality of fish, generated by anaerobic conditions at the bottom of water body and possible anaerobic conditions in the water body as a whole, algae toxicity (VON SPERLING, 2005) as well as being a probable human carcinogen under some conditions (IARC, 2010). Seeking to preserve water resources and prevent further negative impacts, effluent should be treated and their pollutants removed in order to adjust the release to a desired quality or standard of prevailing quality, while always considering the treatment efficiency (VON SPERLING, 2005; CAVALCANTI, 2012). Several scientific studies have reported technologies for nitrate removal from contaminated waters. However, among the various techniques used for the removal of metal ions in water many of them are ineffective or expensive, and often the technology that stands out is the adsorption, because it is highly effective, inexpensive, flexible and simply in process and of easy operation (RAFATULLAH et al., 2010; POPURI et al., 2009).

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The adsorption is the process of separating organic and inorganic substances that are in solution on the interface between a liquid and a solid (CAVALCANTI, 2012), it can be used for such process a diversity of raw materials: silica materials organically functionalized (HAMOUDI; BELKACEMI, 2013), wheat straw resin stratified (XU et al., 2013), cationic polymer-modified granular activated carbon (CHO et al., 2011), ion exchange resin (HEKMATZADEH et al, 2013), lignocellulosic agricultural waste and rice husk (ORLANDO et al., 2002), bamboo powder activated (MIZUTA et al., 2004), modified rice husk (KATAL et al., 2012), invasive species biomass converted into activated carbon (NUNELL et al., 2012), sepiolite, sepiolite activated with hydrochloric acid, boiler slag and activated carbon powder (ÖZTÜRK; BEKTAŞ, 2004). The adsorptive process may be even more promising when natural adsorbents produced from biomass are used (COELHO et al., 2007) because they are renewable, low cost, highly available, and in many cases their disposal becomes an environmental problem (GIRALDO; MORENO-PIRAJÁN, 2008; HAMEED; DIN; AHMAD, 2007). In addition, these materials can be converted into high value-added adsorbents: activated carbons, making it a cleaner source - by replacing fossil carbon sources - and a highly effective material for the removal of pollutants (NOR et al., 2013), very used in sewage treatment (TREVIÑO-CORDERO et al., 2013). Thus, studies relating the use of biomass that can be modified in order to take his job as adsorbents in order to reduce the impacts to the environment and add value to co-products are of great scientific and economic interest. In this context is the bagasse from sugar cane, generated from the juice extraction in the manufacture of sugar and alcohol, and highly available in Brazil, as it is one of the four countries that supplies the international trade in sugar (SEAB, 2013). According to the National Supply Company (CONAB, 2013a) in the 2012/2013 crop it was produced 588,915,700 tons of sugar cane. Considering the relationship bagasse / sugar cane estimated at 29.13% by CONAB (2013b), only in this harvest approximately 171.5 million tons of sugarcane bagasse have been generated. However, despite its wide availability, bagasse is a residue of low exploration in the country (BATTISTELLE; MARCILIO; LAHR, 2008) which makes it very interesting to conduct studies, including regarding the activation of this residue for later use as adsorbent in removing pollutants such as nitrate. Emphasizing that this use can add value to the residue and reduce negative environmental impacts. Therefore, the aim of this study is to assess the parameters that influence the nitrate adsorption process using activated carbon as adsorbent obtained from sugar cane bagasse.

Material and Methods

The experiment was performed at the Instrumental Analysis Laboratory of the Pontifical Catholic University of Parana, Toledo Campus. The sugar cane bagasse was obtained from a farm in the municipality of Toledo – PR, it was dried at 60°C for 48 hours, crushed in a grinder to further homogenization of particle size between 20 and 48 mesh. A physical-chemical modification of the material was carried out by a chemical activation with phosphoric acid solution 3 mol L^{-1} in proportion 5 mL g^{-1} of adsorbent. Subsequently the material was placed in a muffle at 180°C for one hour, increasing to 480°C for a further hour. The temperature rise is intended to produce more pores, which can raise sorptive rates (CAVALCANTI, 2012). After cooling, the material was thoroughly washed with ultrapure water for subsequent filtering and drying at 105°C up to constant weight and obtaining cane bagasse modified (CBM).

Study of Point of Zero Charge

The pH_{PCZ} was determined, also called the point of zero charge of the CBM, which is the pH at which the resultant of the adsorbent surface charge is null. To this was added 0.5 g of modified sugarcane bagasse (CBM) in 50 mL of an aqueous solution of potassium chloride (KCl) 0.5 mol L^{-1} in initial pH values from 1 to 9, adjusted with a solution of hydrochloric acid HCl (0.1 mol L^{-1}) and sodium hydroxide (NaOH 0.1 mol L^{-1}). After three hours of stirring in a water bath thermostatted, the final pH of each solution was obtained, resulting in a graphic change in pH as a function of final pH, considering that the pH_{PCZ} point will be the point which reaches the null value variation (MIMURA et al, 2010, p. 1280).

Kinetics of Adsorption

In order to determine the influence of contact time in the adsorption process, it was added 0.5 g of CBM and 50 mL of KNO_3^- solution in a concentration of 25 mg L^{-1} and pH 4.0 in the Erlenmeyer flask and placed it in stirred at 200 rpm at 25°C in Dubnoff for different times – they were 10, 20, 30, 40, 50, 60, 70, 80 and 90 minutes – in triplicate. Then, 25 mL of the samples was filtered and the concentration of nitrate (NO_3^-) at equilibrium (C_{eq}) by spectrophotometry at 220 and 275 nm wavelength was determined according to Standard Methods (2012). From this value obtained, the amount adsorbed was calculated at equilibrium using Equation 1 below.

Equation 1. Amount adsorbed at equilibrium

$$Q_{eq} = \frac{(C_0 - C_{eq})}{m} \cdot V \qquad (1)$$

In Equation 1, Q_{eq} is the amount of adsorbed ions per unit adsorbent at equilibrium (mg g^{-1}), m is the mass of adsorbent used (g), C_0 represents the initial concentration of nitrate ion in solution (mg L^{-1}), C_{eq} is the concentration of nitrate ion in solution at equilibrium (mg L^{-1}) and V is the volume of solution used (L).

The percentage ion removal was calculated using Equation 2:

Equation 2. Porcent removal of nitrate

$$\%R = 100 - \left(\frac{C_{eq}}{C_0} \cdot 100 \right) \qquad (2)$$

In this equation,%R is the percentage of removal of the ion by the adsorbent, C_{eq} is the concentration at equilibrium of nitrate ion (mg L^{-1}) and C_0 is the initial concentration of nitrate ion in solution (mg L^{-1}). After these calculations the obtained results were linearized by the mathematical models pseudo-first-order, pseudo-second order, Elovich and intraparticle diffusion.

Adsorption Equilibrium

To obtain the isotherms of nitrate adsorption by the CBM tests were performed in which the system conditions were based on ideal conditions found in previous tests, such as the contact time. Thus, there were added 0.5 g of adsorbent and 50 mL of KNO_3^- solution with different concentrations – 5, 10, 15, 20, 25, 30, 35, 40 mg L^{-1} – in triplicate in Erlenmeyer flasks, and the samples were kept in system Dubnoff shaking at 25°C for 30 minutes. After this procedure samples were removed and filtered to determine the concentration of nitrate in solution by spectrophotometry (STANDARD METHODS, 2012). With these results the values of the Q_{eq} and the percentage removal were calculated, and they were linearized by mathematical models of Langmuir, Freundlich and Dubinin-Radushkevich.

Thermodynamic of Adsorption

For this study it was added 0.5 g of sorbent and 50 mL from the solution of KNO_3^- in concentration of 25 mg L^{-1} and pH 4.0 in Erlenmeyer flasks and they were accommodated in a Dubnoff shaking at different temperatures – 25, 35, 45 and 55°C – in triplicate. Samples were filtered to determine the concentration of nitrate in solution by spectrophotometry (STANDARD METHODS, 2012) to check the ideal temperature. With these results some thermodynamic parameters were calculated.

3. Results and Discussion

Obtainment and Characterization of Adsorbent Material

During the modification of sugar cane bagasse the efficiency of the process was evaluated as shown in Table 1, where the efficiency of obtaining the CBM was upper to 60% under the conditions evaluated.

Table 1 - Efficiency of Modified Bagasse from cane Sugar Process

Repetition	Mass of sugar cane bagasse (g)		Process Efficiency (%)	
	Before heating	After heating	Repetition	Average
1	153,384	97,482	63,55	63,48
2	157,697	102,510	65,00	
3	145,862	90,247	61,87	

On Picture 1 there are images of dry sugar cane bagasse (a), triturated (b) and physico-chemical post-modification (c).

Picture 1: Bagasse from Sugar Cane After Drying (A), after Trituration in a Mill (B) and After the Procedure of Physico-Chemical Modification (C)
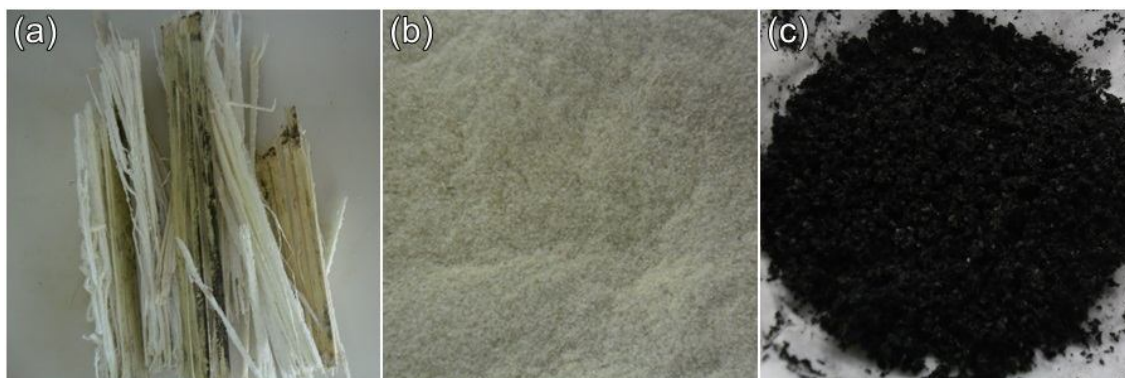
Regarding the study of pH$_{PCZ}$ (Graph 1), it is observed that the point of zero charge occurs in 1.06 (MIMURA et al, 2010).

As Tagliaferro et al. (2010), the adsorption of cations is favored at pH higher than pH$_{PCZ}$, while the adsorption of anions is favored in pH lower than pH$_{PCZ}$. Thus, the adsorption of NO$_3^-$ would be favored by pH less than 1.06, but it is not common to find effluents with such pH, then it was choose pH 4.0 to perform the further studies.

Graph 1: Results of Study of the Point of Zero Charge for the Modified Sugar cane (CBM), Showing the Relationship between the Initial pH and the pH Variation
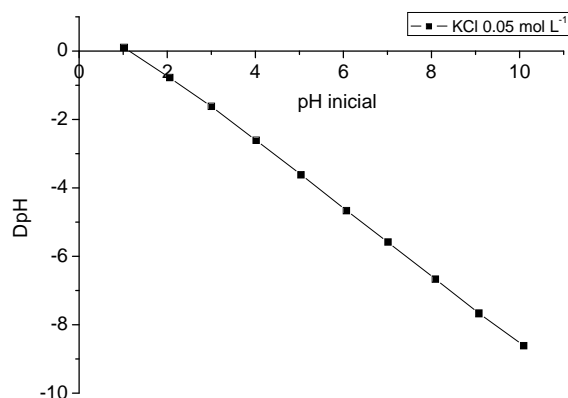
Kinetics of Adsorption

It is observed in Graph 2 the variation of adsorption rate along the contact time between adsorbent/adsorbate.

Graph 2: Results of the Study of Adsorption Kinetics of Nitrate using Modified Sugar cane Bagasse (CBM), Showing the Relationship between the amount Adsorbed at Equilibrium and the Contact Time
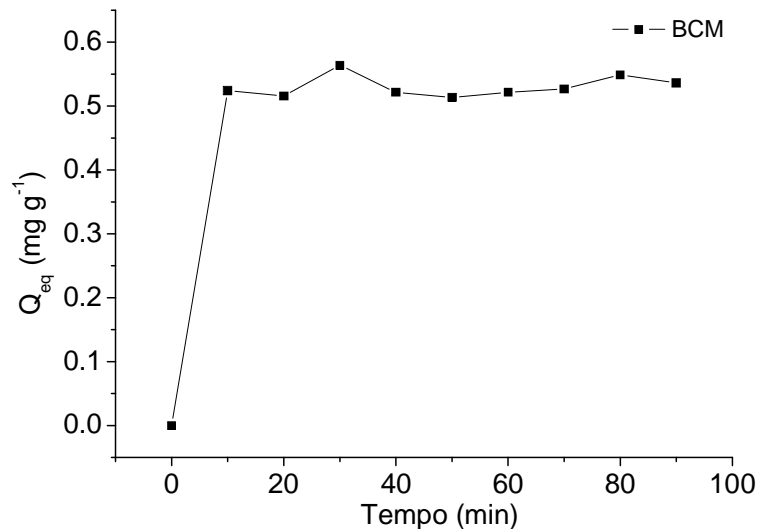
It is observed that the maximum adsorbed amount was obtained in 30 minutes, with this being the ideal time for the realization of the other tests. This time interval is remarkable, as in the case of large-scale treatments with the need for shorter liquid holding time the volume of the reactor can also be reduced (VON SPERLING, 2005) reducing implantation costs. These results were linearized by mathematical models of pseudo-first order, pseudo-second order, Elovich and intra-particle Diffusion, and the results are shown in Table 2.

Table 2: Kinetic Parameters Obtained in the study of NO_3 Adsorption by Modified Sugar cane Bagasse to the Models of Pseudo-First Order, Pseudo-Second Order, Elovich and Intra-Particle Diffusion

| Pseudo-first order			Pseudo-second order			Experimental value	
K_1 (min^{-1})	Q_{eq} (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	Q_{eq} (mg g^{-1})	R^2	Q_{eq} (exp) (mg g^{-1})	
-0,0046	0,0506	0,303	2,6873	0,5388	0,997	0,5302	
Elovich			Intra-particle diffusion				
α (mg g^{-1} h^{-1})	β (g mg^{-1})	R^2	Straight-lines	K_{id} (g mg^{-1} min$^{-1/2}$)	C_i (mg g^{-1})	R^2	
			A	-0,0016	0,5274	0,0339	
0,3965	0,0318	0,466	B	0,1776	0,385	0,8274	

Note: K_1: rate constant of pseudo-first order; Q_{eq}: amount of adsorbate retained per gram of adsorbent at equilibrium; R^2: coefficient of determination; K_2: rate constant of pseudo-second order; Q_{eq} (exp): amount of adsorbate retained per gram of adsorbent at equilibrium experimentally determined; α: constant for the initial rate of the Elovich equation; β: Elovich constant related to the extent of coverage of the activation energy surface for chemisorption; K_{id}: intra-particle diffusion constant; C_i:suggests the thickness of the boundary effect.

According to Radhika and Palanivelu (2006) kinetic models of pseudo-first and pseudo-second order are applicable when the coefficient of determination (R^2) has a value close to 1, and the value of calculated Q_{eq} is near to the experimental Q_{eq}. Therefore, only the pseudo-second order model is applicable, suggesting that the speed mechanism is the chemical adsorption (SPINELLI; LARANJEIRA; FÁVERE, 2005). The Elovich and intraparticle Diffusion models are also not applicable in this study because they had low R_2 values (FEBRIANTO et al., 2009).

Adsorption Equilibrium

Graph 3 shows the NO_3 adsorption rate as a function of the initial concentration.

Graph 3: Results of the Study of the Adsorption Equilibrium of Nitrate Using Modified Sugar cane Bagasse (CBM), Showing the Relation between the Initial Concentration and the Amount Adsorbed at Equilibrium
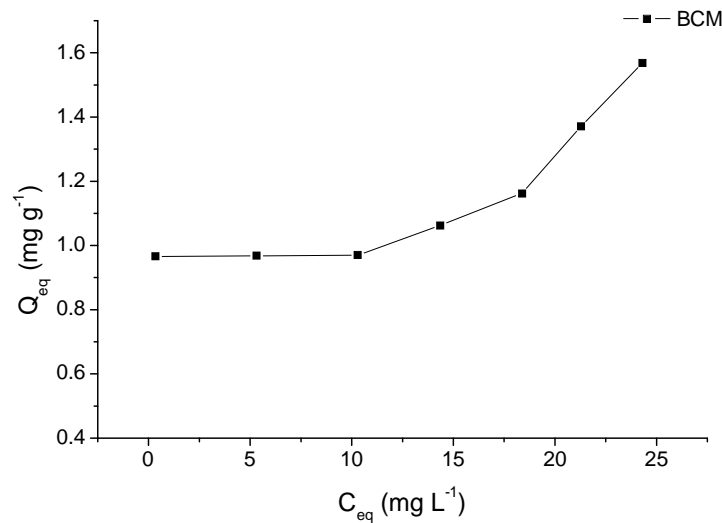
The convex isotherms are called unfavorable because of their low removal capacity in low concentrations. Unfavorable isotherms are rare, but very important to understand the regeneration process, that is, mass transfer from the solid back into the fluid phase, when the isotherm is favorable (McCABE et al., 2005). In Table 3 the values obtained in the construction of the isotherms are observed, these values were used for the linearization by mathematical models of Langmuir, Freundlich and Dubinin-Radushkevich.

Table 3: Results of the Study of Nitrate Adsorption Equilibrium using Modified Sugar cane Bagasse (CBM), Showing Values of Initial Concentration of the Solution, Remaining Nitrate Concentration at Equilibrium (C_{eq}), Adsorbed Amount at Equilibrium and Percentage of NO_3 removal

Initial Concentration (mg L^{-1})	Average C_{eq} (mg L^{-1})	Average Q_{eq} (mg g^{-1})	Removal (%)
5	0,00 ± 0.00	0,50 ± 0.00	100,00
10	0,34 ± 0.14	0,97 ± 0.01	96,60
15	5,33 ± 0.17	0,97 ± 0.02	64,50
20	10,30 ± 0.34	0,97 ± 0.03	48,48
25	14,37 ± 0.13	1,06 ± 0.01	42,53
30	18,38 ± 0.42	1,16 ± 0.04	38,75
35	21,29 ± 0.46	1,37 ± 0.05	39,17
40	24,31 ± 1.08	1,57 ± 0.11	39,22

It is observed that the rate of adsorption at equilibrium increased as the initial concentration was increased. But these increases are not proportional, whereas at higher concentrations the removal percentage was lower, which is noted in Table 3. Therefore it was observed that the best adsorption/removal rate occurred at initial concentrations of 5 and 10 mg L^{-1}, in other words, at lower concentrations. Furthermore, the values obtained at equilibrium studies were placed at linear models of Langmuir-Freundlich and Dubinin Radushkevich shown in Table 4.

Table 4: Parameters Obtained in the Study of Adsorption of NO_3 by Modified Sugar cane to the Models of Langmuir, Freundlich and Dubinin-Radushkevich

| Langmuir				Freundlich			Dubinin-Radushkevich		
Q_m (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	K_f (L mg^{-1})	n	R^2	Q_d (mol g^{-1})	E (kJ mol^{-1})	R^2
18,502	-0,3148	-0,016	0,87	26,309	1,125	0,99	0,0002	9,509	0,855

Q_m: maximum adsorption capacity; K_L: constant related to the strength of adsorbent/adsorbate interaction; R_L: Langmuir constant; R^2: coeficiente of determination; K_f: Freundlich constant of equilibrium; n: related to the heterogeneity of the solid; Q_d: maximum adsorption capacity; E: average power of sorption.

According to the results of R^2, it could be seen that the models of Langmuir Dubinin-Radushkevich do not explain the obtained results, while the best model is the Freundlich one, which indicates that the adsorption process occurs multilayer and in homogeneous surfaces (DAIFULLAH; GIRGIS; GAD, 2003). The *n* represents the spatial distribution of energy sites, values greater than 1 suggest the presence of highly energetic sites (INSKEEP; BAHAM, 1983 apud SODRÉ; LENZI; COSTA, 2001).

Thermodynamics of Adsorption

In Graph 4 it is possible to see the variation in the rate of adsorption of nitrate as a function of the system temperature.

Graph 4: Study Results of Nitrate Adsorption Thermodynamics using Bagasse from Modified sugar cane (CBM)
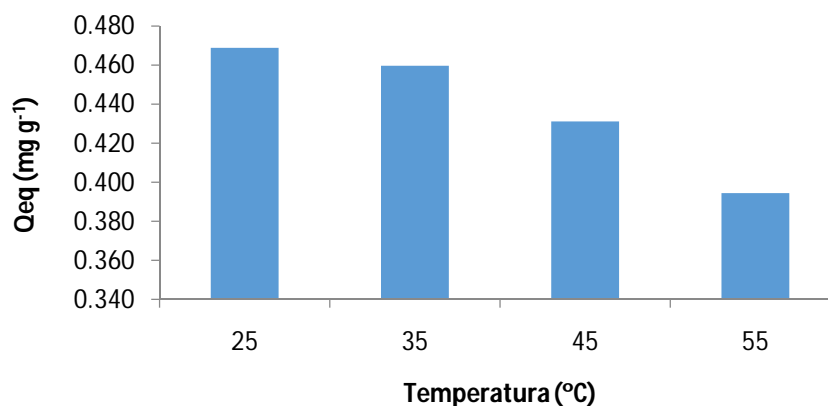
With this study it can be seen that the temperature increasing significantly interferes in the results of nitrate adsorption in modified sugar cane bagasse, while higher temperatures result in smaller amount of adsorbed nitrate. This can also be observed in the values of Q_{eq} showed in Table 5 along with the results for the thermodynamic parameters.

Table 5: Thermodynamic Parameters Obtained in the Study of Nitrate Adsorption by Modified Sugar cane (CBM)

Temperature (°C)	Thermodynamic Parameters				
	Q_{eq} (mg g^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1})	R^2
25	0,469	0,973	7,486	-3,242	0,98
35	0,460	1,006			
45	0,431	1,038			
55	0,394	1,071			

Q_{eq}: amount of retained adsorbate per gram of adsorbent at balance; ΔG: variation of Gibbs free energy; ΔH: enthalpy change; ΔS: entropy change; R^2: determination coefficient.

The variation of Gibbs free energy, ΔG, is the fundamental criterion of process spontaneity, while values below zero indicate spontaneity in certain temperature (ARAUJO et al., 2009). But all obtained values were positive, demonstrating the non-spontaneous in the adsorptive process studied for this adsorbent. As for ΔH, the fact of being positive indicates that the adsorption was an endothermic process (SPEIGHT; ÖZÜM, 2002), and its value, less than 40 kJ mol^{-1} indicates that the nature of adsorption is physical, with weak links between NO_3^- and CBM (ARAUJO et al., 2009). The value of ΔS is related to variations of order-disorder in a system. The more random the system is, the greater its entropy. Negative values of ΔS suggest a reduction of randomness at the solid-solution interface during adsorption (ARAUJO et al., 2009), as occurred in this study.

Conclusions

The results of the kinetic study indicated that the maximum adsorbed amount occurred in the time of 30 minutes, a relatively short space of time, which can reduce deployment costs of a treatment system according to the study. Furthermore, despite the use of a pH that favored the adsorption of cations, the results were satisfactory, removing high percentages (near 100%) of NO_3^- of solutions with low initial concentrations. The studies have shown that the adsorptive process is endothermic and not spontaneous. As the adsorption mechanism the pseudo-second order suggested chemical adsorption. One of the positive aspects of the study is the possibility of using a residue of agribusiness - generated in large quantities in the country, but with little use - the removal of nitrate in water contaminated with nitrate.

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