

# KINETIC AND EQUILIBRIUM ADSORPTION OF XYLENE BY COMMERCIAL ORGANOCCLAY IN LIQUID PHASE

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**ABSTRACT:** The adsorption characteristics of xylene from aqueous solutions by organoclay (Spectrogel, type C) were investigated. In the kinetics studies, it was observed that the process comes into equilibrium after 50 min and the maximum percentage removal was approximately 96% for the three initial concentrations. The obtained data for kinetics adsorption were also fitted through the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The correlation coefficients values ( $R^2$ ) showed that the adsorption kinetic described well by the pseudo-second-order model. The experimental data were analyzed by Langmuir, Freundlich, SIPS and D-R isotherm models. The results indicated that the data were best fitted with the D-R isotherm. The thermodynamic study also indicated that the uptake of xylene by the adsorbent was spontaneous, endothermic and favorable at higher temperatures.

**KEYWORDS:** organoclay; xylene; liquid-phase adsorption; remediation of contaminated soils.

## 1. INTRODUCTION

Water pollution due to industrial development has been a serious problem for many years. The petroleum and petrochemical industries when performing the extraction and refining processes generate large amounts of waste contaminated with organic compounds. Besides these, the automotive and chemical industries also has considerable potential for generating such waste. However, the major source of origin of such waste is due to gasoline leakage from storage tank, transportation and pipelines (Hernández et al., 2005; Tiburtius et al., 2005). Many toxic organic compounds are present in these effluents, such as hydrocarbons of high molecular mass which are difficult to remove, known as benzene, toluene and xylene (BTX). They have been used in solvents and exist in many fuels (Su et al., 2010).

Particularly for Brazilian legislation, The National Council for the Environment, known for acronym CONAMA in Brazil, recently launched the Resolution N° 430 of 13 May 2011 establishing the concentration limits of organic compounds in industrial effluent to receiving bodies. These limits

were 1.2 ppm for benzene and toluene and 1.6 ppm for xylene.

Several processes can be used to treat these types of contaminants, however, new techniques for treating these effluents are emerging in order to adapt to this legislation. One such technique is the adsorption of contaminants in organoclays. This treatment becomes very effective when needed to obtain final concentrations too low (Paiva and Morales, 2012; Peng et al. 2012). Therefore, the aim of this study is to evaluate the potential of a commercial organoclay (Spectrogel® Type C, kindly provided by Spectrochem) for wastewater treatment contaminated with xylene.

## 2. MATERIALS AND METHODS

The commercial organoclay used in this study was kindly provided by Brazilian company SpectroChem. In all investigation steps, the concentration of the xylene in the solution before and after sorption was determined using High Performance Liquid Chromatography (HPLC) (Shimadzu LC-10AD). The mobile phase used consisted of the 28 % of acetonitrile, 35 % of methanol and 37 % of Milli-Q water, at a flow of



1.0 mL/min. The column used was C18 and the wavelength of 204 nm. For preparation of adsorbent, this was sieved for 20 minutes, being used the fraction between sieves of 24 and 28 Tyler mesh to obtain 0.655 mm average particle size diameter.

### 2.1. Effect of pH

The effect of pH on uptake capacity of the commercial organoclay for the xylene was obtained by stirring 5 g of commercial organoclay in each bottle in a total of 4 bottles, containing 500 mL of xylene solution of initial concentration 0.9 mmol.L<sup>-1</sup> at different solution pHs ranging from 4.0 to 12.0 for 5 h. During this process the pH was monitored and controlled at the desired value using reagents NaOH (2 N) and HCl (2 N).

### 2.2. Kinetics and modeling of Adsorption

Adsorption kinetic experiment was carried out by continuously stirring at 200 rpm the amount of 2.5 g of commercial organoclay with 250 mL of xylene solution having three different initial concentration, 0.6, 1.2 and 1.6 mmol.L<sup>-1</sup>, at 298.15 K and initial pH of 6.4. The measured points of sorption were between 0.5 and 300 min. The removal percentage is calculated by Equation 1:

$$\%R = \frac{(C_i - C_f)}{C_i} * 100 \quad (01)$$

where %R is the removal percentage,  $C_i$  and  $C_f$  are the initial and the final concentration of xylene solution, respectively, (mmol.L<sup>-1</sup>).

The principle behind the adsorption kinetics involves the search for a best model that well represents the experimental data. Many kinetic models are available to understand the behavior of the adsorbent and also to examine the mechanism of the adsorption process. In this study, the adsorption data were analyzed using three simplest kinetic models:

- The pseudo first order that is determined from the following expression given by Lagergren (1898);

- The pseudo second order kinetic models, it is given by Ho and McKay (1998) and

- Intraparticle diffusion by Weber and Morris (1963).

### 2.3. Effective diffusion coefficient

For determination of the effective diffusion coefficient was used Boyd kinetic model. This model predicts whether the main resistance to mass transfer is located in the thin film (boundary layer) surrounding the adsorbent particle, or is due to the resistance to diffusion inside the pores.

The effective diffusion coefficient,  $D_i$  (cm<sup>2</sup>.s<sup>-1</sup>), is calculated using the relation:

$$B = \pi^2 * \frac{D_i}{r^2} \quad (02)$$

where  $r$  represents the radius of the particle calculated by sieve analysis and by assuming as spherical particles and  $B$  is given by Boyd et al. (1947).

### 2.4. Equilibrium Studies

The equilibrium experiments were carried out by contacting 1 g of commercial organoclay with 100 mL of xylene solutions having different initial xylene concentrations (0.05 to 1.7 mmol.L<sup>-1</sup>). The samples were agitated in water bath at a constant 200 rpm speed for 3 h at three different temperatures, 288.15 K, 298.15 K and 308.15 K. The amount of xylene adsorbed onto the commercial organoclay at equilibrium was calculated from the mass balance of the Equation 3 as given below:

$$q_e = (C_0 - C_e) * \frac{V}{W} \quad (03)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentration of xylene solution (mmol.L<sup>-1</sup>), respectively,  $q_e$  is the equilibrium xylene concentration on commercial organoclay (mmol.g<sup>-1</sup>),  $V$  the volume of the xylene solution (L) and  $W$  is the mass of commercial organoclay used (g).

The adsorption equilibrium is established plotting solid phase concentration against liquid phase concentration graphically; it is possible to depict the equilibrium adsorption isotherm. There are many theories relating to adsorption equilibrium, in this study the equilibrium data are analyzed using four isotherms, Langmuir (1918), Freundlich (1906), Sips (1948) and Dubinin-Radushkevich (Dubinin, 1960).



## 2.4. Thermodynamic Studies

The amounts of adsorption of BTX were determined in three different temperatures, 288.15 K, 298.15 K and 308.15 K. The following Equations 4 and 5 have been applied to determine the thermodynamic parameters including enthalpy ( $\Delta H_{ads}$ ), Gibbs free energy ( $\Delta G_{ads}$ ), and entropy ( $\Delta S_{ads}$ ).

$$\Delta G_{ads} = -R * T * \ln K_E \quad (04)$$

$$\ln(K_E) = \frac{\Delta S_{ads}}{R} - \frac{\Delta H_{ads}}{R} * \frac{1}{T} \quad (05)$$

where  $K_E$  is the distribution coefficient for the adsorption,  $T$  is the solution temperature (K) and  $R$  is the gas constant.

## 3. RESULTS AND DISCUSSION

Adsorption of xylene onto commercial organoclay was systematically investigated by studying the effect of various parameters such as pH, temperature, and initial organoclay concentration.

### 3.1. Effect of pH

Adsorption of xylene by commercial organoclay is somewhat dependent upon the pH. The effect of pH of the xylene solution on the adsorption capacity of the organoclay is presented in Figure 1.

Figure 1 shows that for different values of pH of the xylene solution there is a little difference on the amount adsorbed. This parameter did not influence on the adsorption of xylene. Brandão et al. (2010) also states that the pH is not so much an important variable in the study of adsorption of hydrocarbons. Furthermore, addition of reagents (acids or bases) to control pH provokes changes on the structure of the organoclay so that it becomes like mud, and therefore cannot be applied in dynamic system (porous bed). The result shown in Figure 1 at pH 10 indicates the natural pH of the system, i. e., without control thereof.

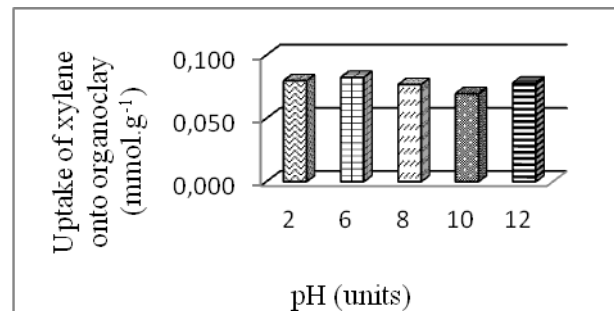


Figure 1. Effect of pH.

### 3.2. Kinetics and Effective Diffusion Coefficient

Figure 2 shows the percentage removal of xylene tested for each initial concentration. This percentage removal was calculated by Equation 1.

The process comes into equilibrium after 50 min for the three initial concentrations. This removal can be considered fast when compared with other adsorbents as activated carbon studied by Souza et al. (2012), which can take up to about 800 min to reach equilibrium. According to Cooney (1999), the adsorption kinetics are initially fast because the adsorption process takes place predominantly on the outer surface, followed by a slow adsorption step on the inner surface of the adsorbent. Adsorption is expected to occur faster on adsorbents with lower degrees of microporosity, i.e., those that do not have many pores that are accessible to solute molecules, when compared to adsorbents with a greater number of micropores. The maximum percentage removal (% R) was approximately 96% for the three initial concentrations.

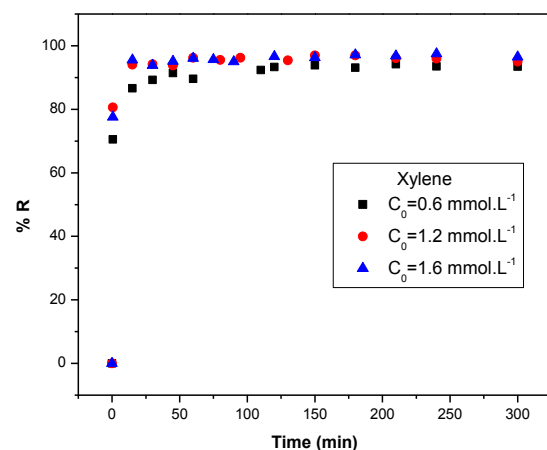
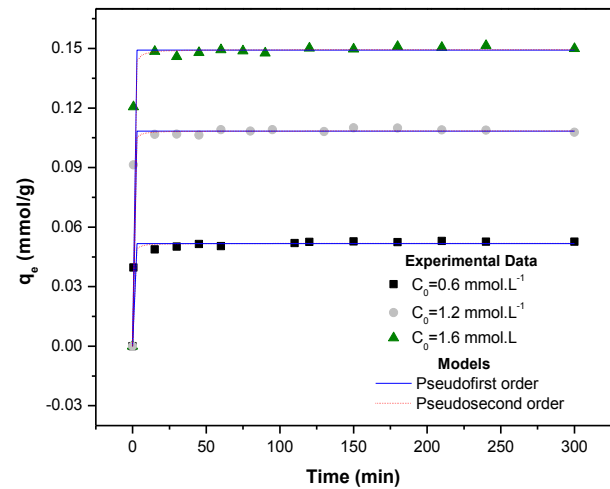


Figure 2: Percentage removal of xylene.



Figure 3 shows the fits of the pseudo first order and pseudo second order models of the kinetics removal and Table 1 exhibits the parameters and coefficient of determination for the fits of the pseudo first order and pseudo second order models. The maximum adsorption capacity was 0.055, 0.11 and 0.15 mmol.g<sup>-1</sup> in initial concentration of 0.6, 1.2 and 1.6 mmol.L<sup>-1</sup>, respectively. From the data presented it can be concluded that this adsorbent material has great affinity for the contaminant and it can be compared with one of the best adsorbent at the moment, activated carbon. Souza et al. (2012) studied the adsorption of monocomponent BTX compounds using activated carbon for an initial concentration of 15 mg.L<sup>-1</sup> of xylene (0.1413 mmol.L<sup>-1</sup>), the concentration of contaminant remaining at equilibrium was 0.7 mg.L<sup>-1</sup> (0.0066 mmol.L<sup>-1</sup>), or that is, the adsorption capacity was 1.43 mg.g<sup>-1</sup> (0.0135 mmol.g<sup>-1</sup>).

It is seen that the correlation coefficient of first-order kinetic model is lower than in the case of second-order kinetic model (Table 1). This shows that kinetic of xylene adsorption by commercial organoclay is better described by pseudo-second order kinetic model rather than pseudo-first order. This was also observed in others studies, such as Moura et al (2011) who studied the adsorption of BTX in monolithic periodic mesoporous organosilica modified and also had good correlation for both models and Nourmoradi et al (2012) who studied the adsorption of BTX in modified montmorillonite nonionic surfactant and adjusted by the pseudo second order model.



**Figure 3.** Adjust the kinetic. of removal of xylene.

For the tests performed at different concentrations can be observed that the constant  $K_2$  varies as the concentration of the adsorptive tests increases. The initial rate constant of adsorption increases with increasing initial concentration. Both indicate that the initial concentration parameter influences the behavior of these constants.

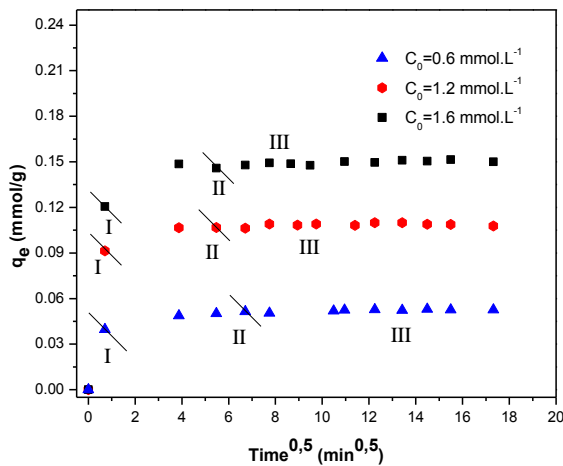
The calculated intraparticle diffusion coefficient,  $K_{dif}$ , and the correlation coefficient are shown in Table 2, together with the constant effective diffusivity Boyd,  $D_i$ . The curve of intraparticle diffusion kinetic indicate that adsorption occurs in three stages as shown in Figure 4.

**Table 1.** Parameters and coefficients of determination of pseudo first order and pseudo second order models for adsorption of xylene.

$C_0$ (mmol.L <sup>-1</sup> )	Pseudo first order			Pseudo second order			
	$q_e$ (mmol.g <sup>-1</sup> )	$K_1$ (min <sup>-1</sup> )	$R^2$	$q_e$ (mmol.g <sup>-1</sup> )	$K_2$ (g.mmol <sup>-1</sup> min <sup>-1</sup> )	$h$ (mmol/g <sup>-1</sup> .min <sup>-1</sup> )	$R^2$
0.6	0.0521	0.2090	0.7545	0.0519	27.2563	0.0734	0.8799
1.2	0.0886	0.2320	0.6398	0.0874	18.1762	0.1388	0.7884
1.6	0.1241	3.0014	0.8949	0.1248	47.8213	0.7448	0.909

**Table 2.** Intraparticle diffusion parameters and effective diffusion coefficient.

$C_0$ (mmol.L <sup>-1</sup> )	Intraparticle diffusion			Boyd	
	$K_{dif}$ (mmol.g <sup>-1</sup> .min <sup>-0.5</sup> )	C	R <sup>2</sup>	$D_i$ (10 <sup>8</sup> . cm <sup>2</sup> .s <sup>-1</sup> )	R <sup>2</sup>
0.6	0.0020	0.0392	0.9360	4.7997	0.8719
1.2	0.0035	0.0900	0.8964	6.0495	0.6599
1.6	0.0039	0.1235	0.7457	11.3664	0.9903



**Figure 4.** Intraparticle diffusion model.

Through the analysis of Figure 4, it is noted that the first stage is completed within 2 min of contact adsorbate/adsorbent. The subsequent step is the diffusion of adsorbate through the pores of the material (intraparticle diffusion), which shows a linear relationship that may indicate that the intraparticle diffusion may be a limiting step of the process. The calculation of  $K_{dif}$  is made in the linear range, so at this stage. The third stage is a slow process due to the low concentration gradient.

The data on the initial concentration of 1.6 mmol.L<sup>-1</sup> did not adjust well to the model. The coefficient of the effective diffusivity is of the

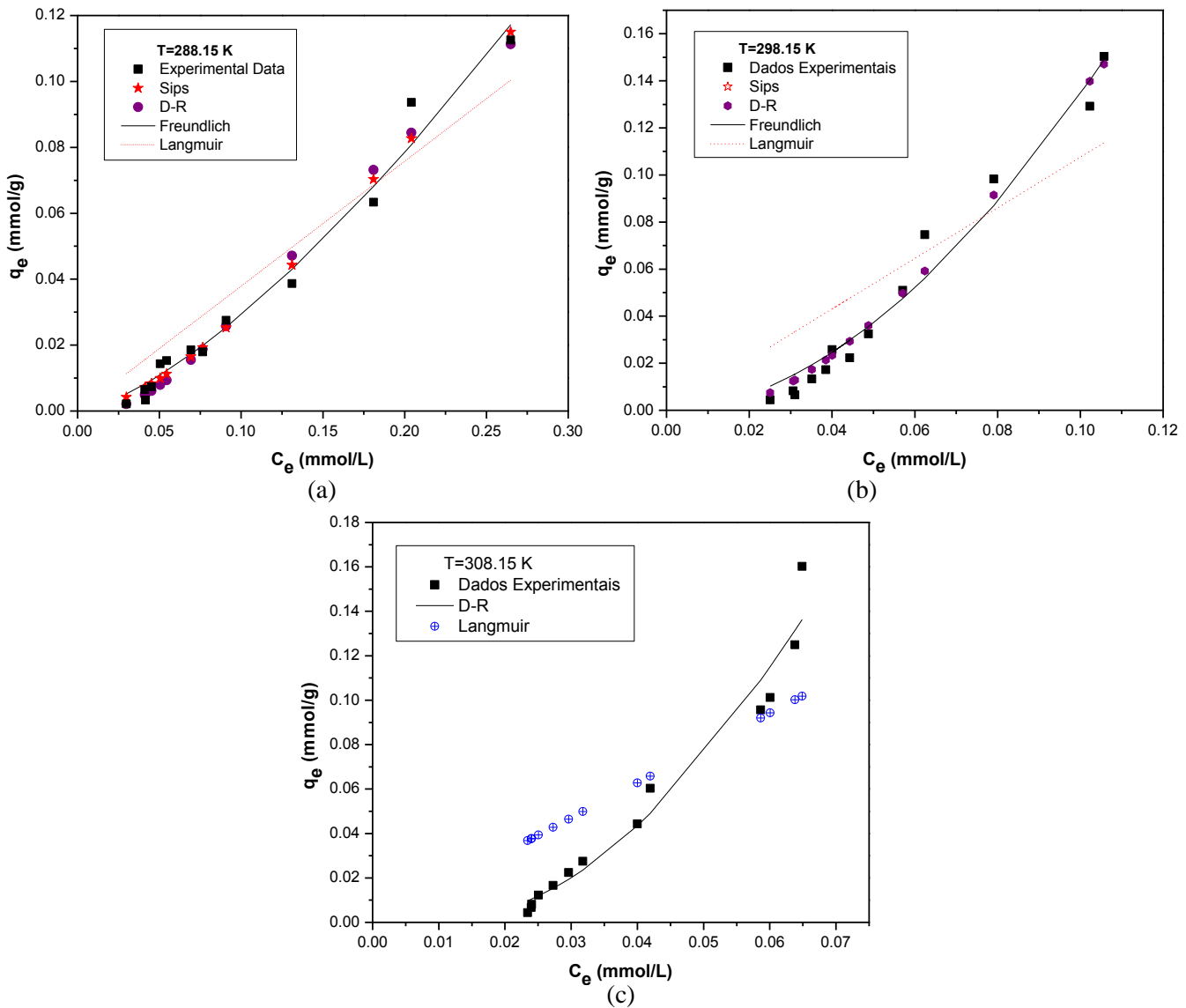
order of 10<sup>-8</sup>. For initial concentration of 1.2 mmol.L<sup>-1</sup>, the Boyd model does not fit well. Souza et al. (2012) also found values in order of magnitude close, 10<sup>-7</sup>. The kinetics of diffusion developed by Boyd (1947) shows that the adsorption process is controlled by both effects, intraparticle diffusion and external diffusion.

### 3.3. Equilibrium Adsorption Studies

The adsorption isotherms of xylene in a liquid phase on organoclay adsorbent at 288.15 K, 298.15 K and 308.15 K are shown in Figure 5. The adjusted models and corresponding parameters are presented in this figure and also in Table 3. For all models were calculated the average relative deviations (ARD) in percentage by Equation 6.

$$ARD = \frac{\sum_{i=1}^n \frac{|q_i^{cal} - q_i^e|}{q_i^e}}{n} * 100 \quad (06)$$

where  $n$  is the number of points used,  $q_i^{cal}$  is the adsorbed amount at equilibrium calculated by the model at each point of the curve  $i$  (mmol.g<sup>-1</sup>) and  $q_i^e$  is the equilibrium amount adsorbed measured experimentally (mmol.g<sup>-1</sup>), for each point  $i$  of the curve.



**Figure 5.** Adsorption isotherms of xylene into commercial organoclay at temperatures of: (a) 288.15 K, (b) 298.15 K e (c) 308.15 K.

**Table 3.** Parameters of the adjustment models of isotherms of xylene.

Models	Parameters	Temperature		
		288.15 K	298.15 K	308.15 K
	$q_e$ (mmol.g <sup>-1</sup> )	<b>0.1126</b>	<b>0.1503</b>	<b>0.1602</b>
Sips	$q_m$ (mmol.g <sup>-1</sup> )	0.4117		
	$K_s$ (mmol.L <sup>-1</sup> )	3.5282		
	$n_s$ (adimensional)	0.6016	-	-
	$R^2$	0.9910		
	<b>ARD (%)</b>	<b>27.4681</b>		
Langmuir	$q_m$ (mmol.g <sup>-1</sup> )	574.5064	6454.9150	8534.7080
	$B$	0.0007	0.0002	0.0624
	$R_L$	0.9999	0.9999	0.9958

	$K_L (L. mmol^{-1})$	0.4021	1.2910	532.5658
	$R^2$	0.9578	0.8827	0.9812
	<b>ARD (%)</b>	<b>102.7911</b>	<b>144.2543</b>	<b>174.1997</b>
Freundlich	$K_F (L. mmol^{-1})$	0.7811	9.6432	-
	$n$ (adimensional)	0.7006	0.5389	
	$R^2$	0.9902	0.9845	
	<b>ARD (%)</b>	<b>34.7523</b>	<b>40.6673</b>	
D-R	$X_m (mmol.g^{-1})$	0.2899	1.0749	3.3612
	$k (mmol^2.kJ^{-2})$	0.0683	0.0588	0.0624
	E	2.7057	2.9160	2.8307
	$R^2$	0.9885	0.9901	0.9812
	<b>ARD (%)</b>	<b>19.457</b>	<b>27.908</b>	<b>24.624</b>

The SIPS model did not fit the data of 298.15 K and 308.15 K. The Langmuir model although fit to the experimental data, showed very high values of DMR. The Freundlich model does not fit the experimental data in the temperature of 308.15 K, but in the others, ARD had values less than 30% and  $R^2$  values close to 1. Overall, the D-R was the only model that fits well at all temperatures and showed lower values of ARD and  $R^2$  values close to 1. The values of parameters E indicate that adsorption is physical. Nourmoradi et al. (2012) also adjusted the data for the adsorption equilibrium of xylene by the D-R model and obtained correlation coefficient equal to 0.836.

### 3.4. Thermodynamic Parameters

The Table 4 shows the thermodynamic parameters for adsorption of xylene.

Generally, the absolute magnitude of the change in free energy for physisorption is between  $-20$  and  $0$   $\text{kJ.mol}^{-1}$  and chemisorption has a range of  $-400$  to  $-80$   $\text{kJ.mol}^{-1}$  (Yu et al. 2001). Hence, this process can be considered as physisorption. The change in energy for adsorption of xylene onto commercial organoclay is  $-19.26$   $\text{kJ.mol}^{-1}$  at 288.15 K,  $-20.84$   $\text{kJ.mol}^{-1}$  at 298.15 K and  $-27.67$   $\text{kJ.mol}^{-1}$  at 308.15 K.

**Table 4.** Thermodynamic parameters for adsorption of xylene onto commercial organoclay.

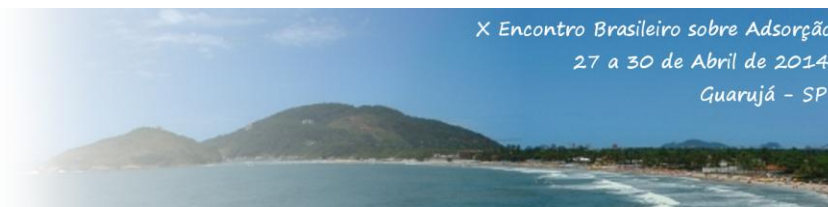
$\Delta H_{ads}$ ( $\text{kJ.mol}^{-1}$ )	$\Delta S_{ads}$ ( $\text{kJ.mol}^{-1}.\text{K}^{-1}$ )	$-\Delta G_{ads}$ ( $\text{kJ.mol}^{-1}$ )			$R^2$
		288.15 (K)	298.15 (K)	308.15 (K)	
100.9652	0.4144	19.2624	20.8436	27.6679	0.8339

The negative values of  $\Delta G_{ads}$  indicate that the adsorption of xylene on the commercial organoclay is spontaneous. It can also be noted that the change in free energy decreases with increase in temperature. The positive value of change in enthalpy ( $\Delta H_{ads}$ ) shows that the adsorption is endothermic in nature and the positive values of  $\Delta S_{ads}$  may indicate an increase in degree of freedom of the adsorbed species. Other authors also studied xylene adsorption and

found values in the same order of magnitude, such as Nourmoradi et al. (2012), who obtained  $\Delta H_{ads} = 28.61$   $\text{kJ.mol}^{-1}$  and  $\Delta S_{ads} = 0.1051$   $\text{kJ.mol}^{-1}.\text{K}^{-1}$ .

## 4. CONCLUSIONS

In this study, commercial organoclay was surveyed to assess its capacity to remove xylene



from aqueous solution. It was found that removal capacity is about 96% with contact time of 50 min between clay and solution of xylene. The adsorption of xylene onto commercial organoclay was well described by the pseudo-second order kinetic and D-R isotherm models. Thermodynamic study showed that xylene adsorption onto the adsorbent was physical, endothermic and spontaneous. Due to its low cost, non-toxicity and adsorption capacity, this adsorbent can be considered as one of the effective options to remove xylene from aqueous solution.

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## 6. ACKNOWLEDGEMENT

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