ADSORPTION OF BENZENE IN AQUEOUS SOLUTION BY COMMERCIAL AND ORGANOPHILIZATED FLUIDGEL CLAY

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ABSTRACT: Contamination of wastewaters with organic compounds such as benzene is becoming an increasingly common problem, leading to the constant interest in techniques to treat these effluents. The adsorption is a very efficient method, with the advantages of the use of alternative adsorbents, like the organoclays. In this work, the organoclay was prepared by sodium smectite clay (Fluidgel) and hexadecyltrimethylammonium bromide salt (HDTMA). The organoclay was characterized by adsorption/desorption of N_2 (BET). Kinetic data were fitted by well known models , and the pseudo second order model better described the experimental data. A removal over 90% of the contaminant with $C_0 = 1.09$ mmol/L was achieved. Among the equilibrium models tested, the isotherm data was better fitted by the DR model. Thus, the organoclay demonstrates great potential for application in the removal of organic compounds.

KEYWORDS: adsorption; benzene; organoclay.

1. INTRODUCTION

Every day, a large amount of wastewater contaminated with organic compounds is generated by various industrial processes. Benzene is one of toxic organic compounds, harmful to health and the environment, with this, their removal from the effluent is of fundamental importance for the environment (Maltoni*et al.,* 1985).

There are countless methods of treatment of these contaminated waters, among which stands out the adsorption, which has been shown an efficient method, adapting to environmental legislation, economically viable and that also presents the advantage of the possibility of regeneration of the adsorbent.

The use of clays as an alternative adsorbent material has been the subject of much scientific research (Amaral *et al*, 2010; Bertagnolli, 2010; Hanna *et al*, 2005), because it is an abundant, easy availability and low cost material in Brazil.

The aim of this study is to evaluate the potential application for removal of organic compounds, especially benzene in aqueous solution by organoclay comparing with the removal in a commercial bentonite clay.

2. MATERIALS AND METHODS

2.1. Preparation of Organoclay

The organoclay was prepared from 100 g of commercial clay Fluidgel with 1 L of deionized water, held under constant agitation for 30 min. Thereafter, 62.59 g of hexadecyltrimethylammonium bromide salt (HDTMA) were added and kept stirring for 4 hours. Then, the solution was filtered and washed with deionized water to remove excess of salt present. Then, the material was dried in an oven at 55 °C for 48 hours, crushed and separated granulometrically.

2.2. Properties of the Adsorbents

To evaluate the process of organophilization by Bedin *et al.* (2013), tests of adsorption / desorption of N_2, with both clays (commercial and organoclay). Physico-chemical properties were obtained, such as specific surface area (Sg), and

the total pore volume (Vp) and the average pore diameter (dp).

2.3. Removal Kinetics

For both clays, the kinetic experiments were conducted using 250 mL of benzene solution with initial concentration of 1.09 mmol / L and 2.5 g of clay with dp = 0.55 mm, which was remained under constant stirring and natural pH (initial value of 10). At time intervals of 30 seconds to 300 minutes, aliquots of solution were collected as described in the work Souza (2013). Subsequently, to verify final concentration of solutions, aliquots were filtered and analyzed by high performance liquid chromatography (HPLC) on a C18 column with a wavelength of 206 nm and a mobile phase of 28% acetonitrile, 35% methanol and 37% of milli-Q water.

The kinetic models applied for the analysis of experimental data were pseudo-first order model, pseudo second-order and intraparticle diffusion.

2.3.1. Pseudo-First-Order Model: The model was proposed by Lagergren*et al.* (1898) and occurs when the determinant step in the rate of adsorption precedes the surface diffusion. Equation 01 describes the model.

$$q_t = q_e.\left(1 - e^{-K_1.t}\right) \tag{01}$$

Where: q_t: amount adsorbed on the solid phase in a time t (mmol.g⁻¹);

q_e: amount adsorbed on the solid phase at equilibrium (mmol.g⁻¹);

K_1: rate constant of adsorption of pseudo-first-order (min⁻¹);

t: contact time (min).

2.3.2. Pseudo-Second-Order Model: Proposed by Ho and McKay (1998), this model describes the reaction adsorbate-adsorbent as the determinant step in the rate for adsorption. Equation 02 describes the model.

$$q_t = q_e.\frac{q_e.K_2.t}{1 + q_e.K_2.t} \tag{02}$$

Where: K_2: rate constant of adsorption of pseudo-second-order (g.mmol⁻¹.min⁻¹).

2.3.3. Intraparticle Diffusion Model: The model proposed by Weber and Morris (1963)

considers the internal diffusion as the determinant step and is described in Equation 03.

$$q_t = K_{dif}.t^{0.5} + C \tag{03}$$

Where: K_{dif}: intraparticle diffusion coefficient (mmol.g⁻¹.min⁻⁰·⁵);

C: constant related to the thickness of the boundary layer (mmol.g⁻¹).

2.4. Adsorption Isotherms

For adsorption isotherms 100 mL of benzene solution were used at concentrations between 0.064 and 3.841 mmol / L with 1 g of clay. The system was stirred continuously for 4 hours at a speed of 300 rpm. The study was conducted at temperatures of 15 ℃, 25 ℃ and 35 ℃. Then, aliquots of solution were removed and analyzed by high performance liquid chromatography (HPLC).

The isotherm models evaluated were the Langmuir, Freundlich, Sips, D-R, DSL and MSAM. However, DSL and MSAM models did not show satisfactory results. Therefore, they were not presented in this paper.

2.4.1. Langmuir Model: The Langmuir model (1918) assumes monolayer adsorption, finite number of identical and homogeneous sites and no interaction between the adsorbed molecules. The model is described by Equation 04.

$$q_e = \frac{q_{max}.K.C_e}{1 + K.C_e} \tag{04}$$

Where: q_e: amount adsorbed on the solid phase at equilibrium (mmol.g⁻¹);

q_{max}: maximum adsorption capacity (mmol.g⁻¹);

K: equilibrium constant of adsorption (L.mmol⁻¹);

C_e: concentration in the liquid phase at equilibrium (mmol.L⁻¹).

2.4.2. Freundlich Model: The Freundlich model (1926) is empirical, assumes monolayer adsorption and not equivalent and / or independent sites. Equation 05 describes the model.

$$q_e = K_F.C_e^{1/n} \tag{05}$$

Where: K_F: equilibrium constant of adsorption capacity (L.mmol⁻¹);

n: constant of intensity adsorption.

2.4.3. Sips Model: The Sips model (1948) considers some of the assumptions of the models of Langmuir and Freundlich. It is quite applied to the adsorption surfaces and in heterogeneous systems is described by Equation 06.

$$q_e = \frac{q_S.K_S.C_e^{1/ns}}{1+q_S.K_S.C_e^{1/ns}} \qquad (06)$$

Sendo: K_S: Sips equilibrium constant (L.mmol⁻¹);

q_S: maximum adsorption capacity for Sips (mmol.g⁻¹);

ns: constant of intensity adsorption to Sips.

2.4.4. Dubinin-Radushkevich Model (D-R): The model is usually applied to the adsorption isotherms in micropores in adsorption systems involving only van der Waals forces and to analyze isotherms with a high degree of rectangularity. The model is described by Equations 07 and 08.

$$\ln(C_S) = \ln(X_m) - k.E^2 \qquad (07)$$

$$E = R.T.\ln\left(1 + \frac{1}{C_e}\right) \qquad (08)$$

Where: E: Polanyi potential;

C_s: concentration of the adsorbate on the adsorbent on the equilibrium (mmol.L⁻¹);

X_m: adsorption capacity (mmol.g⁻¹);

K: constant (mol².kJ⁻²);

R: ideal gas constant (8,314.10⁻³ kJ.mol⁻¹.K⁻¹);

T: temperature (K).

3. RESULTS AND DISCUSSION

3.1. Properties of the Adsorbents

The results of properties for both adsorbents obtained in previous work by Bedin *et al.* (2013) are shown in Table 1. It can be seen that after the process of organophilization, it occurred a decrease in the values of the parameters of clay, which can be attributed to intercalation of organic cations of HDTMA in the structures of the adsorbent. These cations act as pillars, increasing the interlayer spacing of the clay mineral and thus confirms the organophilization process(Wang *et al.* 2004).

**Tabel 1.**Physical/chemical parameters of commercial clay and organoclay.

| Clay	Sg (m²/g)	Vp (cm³/g)	Dp (Å)
Commercial	59,870	0,086	40,170
Organoclay	6,230	0,013	26,640

Source: Bedin *et al.* (2013).

3.2. RemovalKinetics

The data of the kinetics of benzene removal into commercial clay and organoclay, and adjustment curves for pseudo-first order, pseudo-second order and intraparticle diffusion models are shown in Figure 1. The values of the kinetic models parameters evaluated are shown in Table 2.
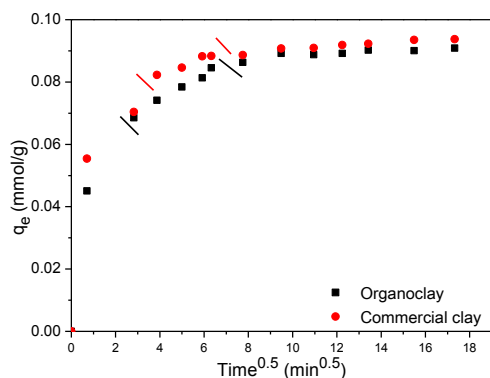
The Fluidgel organoclay shows a potential compared with other adsorbents, such as the activated carbon which obtained 83% of removal of benzene, with C_0 = 1.280 mmol / L. (Luz, 2009).
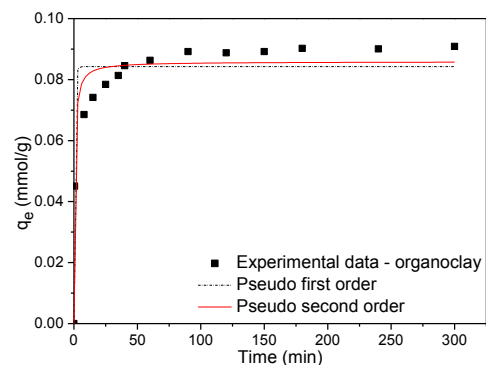
(a) Organoclay
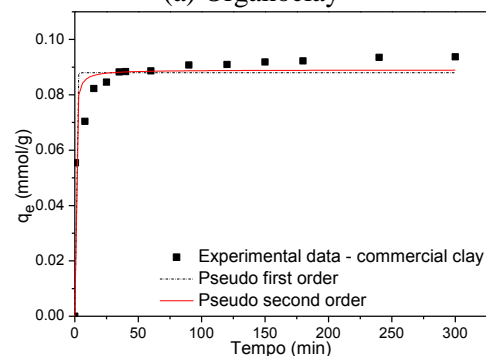
(b) Commercial clay

(c) Intraparticle diffusion

Figure 1. Kinetics of removal and adjustment of pseudo-first order, pseudo-second order and intraparticle diffusion models.

Table 2. Parameters of the models of pseudo first order, pseudo second order and intraparticle diffusion.

	Pseudo-first-order		
Clay	q_e (mmol.g^{-1})	K_1 (min^{-1})	R^2
Org.	0.084	1.530	0.923
Com.	0.088	1.989	0.938

	Pseudo-second-order		
	q_e (mmol.g^{-1})	K_2 (g.mmol^{-1}.min^{-1})	R^2
Org.	0.086	20.999	0.949
Com.	0.089	32.338	0.956

	Intraparticlediffusion		
	K_{dif} (mmolg^{-1}.min$^{-0.5}$)	C (mmol.g^{-1})	R^2
Org.	0.001	0.079	0.976
Com.	0.003	0.077	0.829

Regarding the adjustment of the kinetic model, it was found that the pseudo-second order-model was the best in describing the experimental data, showing high correlation coefficients and proximity of the theoretical value of benzene adsorbed with the value obtained experimentally. Similar results were verified by Souza, Didi and Silva (2011), removing benzene onto red mud; Aivalioti*et al.* (2012), adsorbing BTEX and methyl tertiary butyl ether on natural and modified diatomite; Nourmoradia, Nikaeena and Khiadani (2012) by removing benzene, toluene, ethylbenzene and xylene on modified montmorillonite.
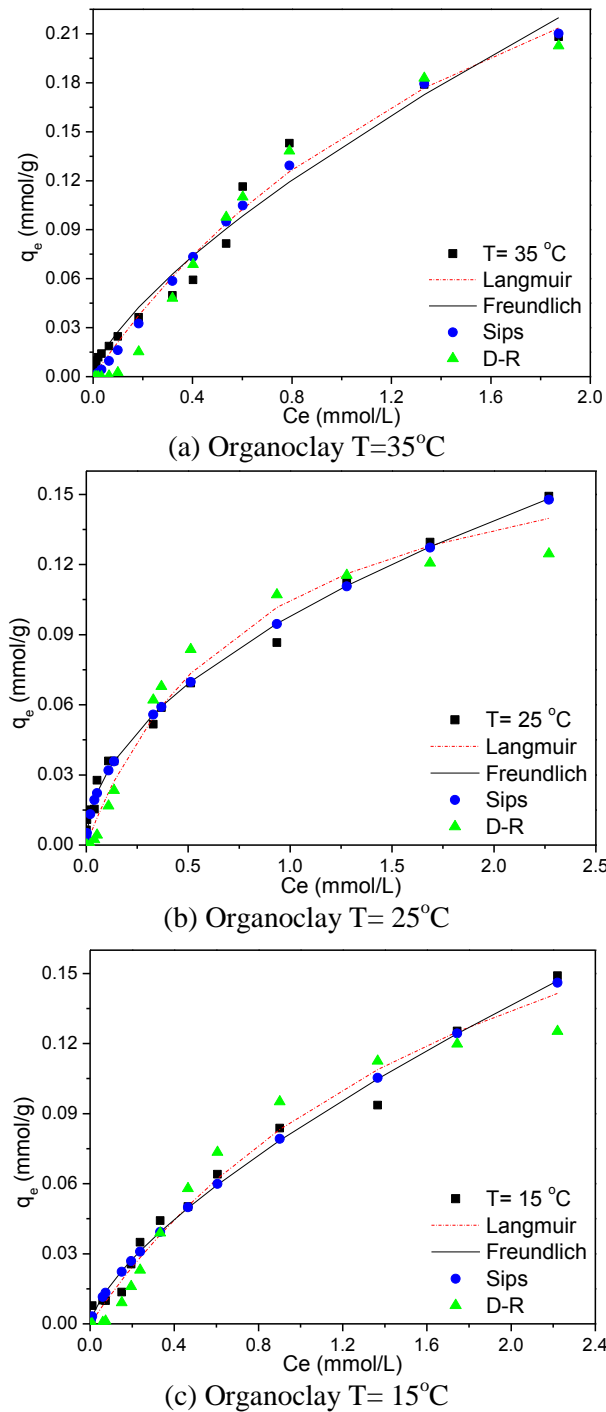
3.3. Adsorption Isotherms

The equilibrium isotherms for commercial clay and organoclay, as well as the adjustments of Langmuir, Freundlich, Sips and D-R models are shown in Figures 2 and 3. The values of the amount of benzene adsorbed and the parameters of the isotherm models applied are shown in Tables 3 and 4.

Analyzing Figures 2 and 3 and Tables 3 and 4, it is observed that the amount of adsorbate removed increases with increasing temperature, suggesting the endothermic nature of the reaction. Similar results were found by Scheider (2008), to remove the organic compound phenol on activated carbon.

Regarding the equilibrium models tested, it is seen that the Langmuir and Freundlich models described satisfactorily only a band of experimental data concerning low concentrations. Thus, there were observed high coefficients of determination and a large discrepancy between the values of the amount of adsorbate removed experimentally and values obtained by these models. Similar results were found by Souza (2013) to adsorb BTX on red mud and Bedin et al. (2013), in removal of the organic compound toluene on organoclay.

The model Sips provided high coefficient of determination, but showed high discrepancy between the amount of adsorbate removed experimentally from the theoretical amount.

(a) Organoclay T=35°C


(b) Organoclay T= 25°C

(c) Organoclay T= 15°C

Figure 2. Adsorption isotherms and adjustment of equilibrium models for the organoclay.

The D-R model better described the experimental data among the models tested, showing high correlation coefficients and proximity of the theoretical values with the experimental parameters. Alves (2013) also obtained good fit to the D-R model in adsorption of malachite green dye on kaolinite and bentonite clays. Brandão et al. (2010) evaluated the models

of Langmuir, Freundlich, Temkin and D-R to fit data of adsorption of petroleum hydrocarbons in sugar cane bagasse, with no success.

(a) Commercial clay T= 35°C

(b) Commercial clay T= 25°C

(c) Commercial clay T= 25°C
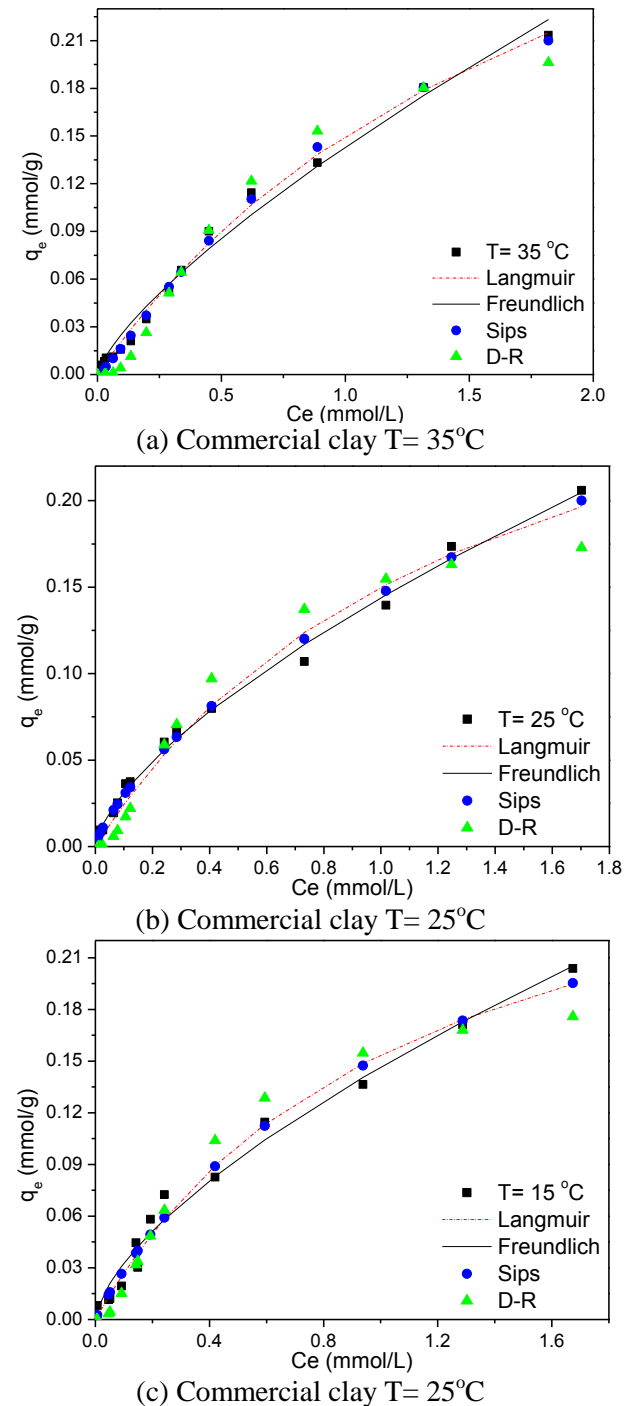
Figure 3. Adsorption isotherms and adjustment of equilibrium models for the commercial clay.
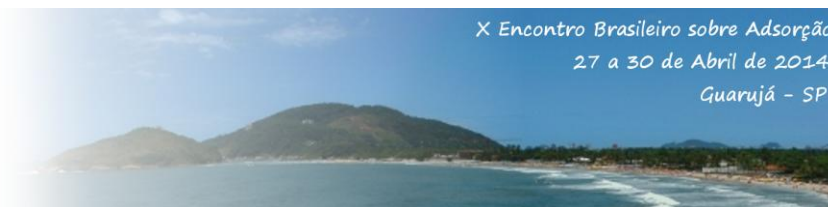
Tabel3 – Model parameters of the isotherms for the organoclay.

Parameters	Temperatures		
	35 ^{o}C	25 ^{o}C	15 ^{o}C
q_e (mmol.g^{-1})	0,208	0,149	0,148
Langmuir			
q_{max} (mmol.g^{-1})	0,436	0,190	0,271
K_L (L.mmol^{-1})	0,512	1,232	0,492
R^2	0,979	0,955	0,984
Freundlich			
K_F (L.mmol^{-1})	0,141	0,098	0,084
n	1,413	1,979	1,440
R^2	0,973	0,992	0,988
Sips			
q_S (mmol.g-1)	0,313	10,755	1,2629
K_S (L.mmol^{-1})	0,943	0,009	0,055
R^2	0,979	0,993	0,988
D-R			
X_m (mmol.g^{-1})	0,234	0,131	0,137
k (mol².kJ^{-2})	0,120	0,062	0,114
R^2	0,963	0,888	0,938

Tabel4 – Model parameters of the isotherms for the commercial clay.

Parameters	Temperatures		
	35 ^{o}C	25 ^{o}C	15 ^{o}C
q_e (mmol.g^{-1})	0,213	0,206	0,204
Langmuir			
q_{max} (mmol.g^{-1})	0,453	0,353	0,322
K_L (L.mmol^{-1})	0,496	0,739	0,912
R^2	0,994	0,982	0,986
Freundlich			
K_F (L.mmol^{-1})	0,143	0,144	0,146
n	1,347	1,504	1,531
R^2	0,986	0,953	0,983
Sips			
q_S (mmol.g-1)	0,316	0,723	0,356
K_S (L.mmol^{-1})	0,957	0,253	0,752
R^2	0,995	0,993	0,987
D-R			
X_m (mmol.g^{-1})	0,222	0,190	0,193
k (mol².kJ^{-2})	0,100	0,071	0,072
R^2	0,978	0,928	0,958

6. CONCLUSIONS

In this study, there was a reduction of the physico-chemical parameters of the adsorbent materials due to the intercalation of organic cations contained in HDTMA, thus confirming the process of organophilization.

The kinetic model that best described the experimental data was the pseudo second order, suggesting the reaction of the adsorbate in the active site of the adsorbent as the determinant step in the rate of adsorption.

The isotherm model which showed the best fit to the experimental data was the Dubinin-Radushsevich.

Finally, the organoclay seems to be a viable adsorbent for the removal of benzene from contaminated effluent, especially in fixed bed systems in function of its low extensibility in aqueous solution.

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8. ACKNOWLEDGEMENT