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Fluid-dynamic Study of Benzene Adsorption from Liquid Phase by Commercial Organoclay

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The aim of this study is to investigate the influence of operating flow rate in fixed bed adsorption of benzene, present in low concentration in aqueous solution, on particles of commercial organoclay. The fixed bed has 6.5 cm in height and 0.65 cm in internal diameter and was filled with about 2.0 g of adsorbent. The average diameter of organoclay particles was of 0.655 mm and the adsorption equilibrium and breakthrough curves were determined at flow rates of 5, 10 and 20 mL.min^{-1}. The experiments were performed at room temperature (25 ^{o}C) and the initial concentration of benzene in liquid phase was 1.2 mmol.L^{-1}. The adsorption efficiency and mass transfer parameters (total amount of sorbate removed, useful amount removed until the rupture point, height of mass transfer zone and total removal percentage) were used in order to evaluate the removal of hydrocarbon from water in the experiments. The higher removal of 1.431 mmol.g^{-1} was obtained with the highest flow rate of 20 mL.min^{-1}. The model developed by Yan, Thomas and Clark reproduced adequately all the breakthrough curves and the experimental data. In this work we concluded that the organoclay has higher adsorption capacity than other alternative materials for adsorption of organic compounds.

1. Introduction

The quality of water on the planet is subject of much concern because its indiscriminate use and contamination of water bodies are committing human supply. The water that reaches the taps of the population may be contaminated by chemicals or harmful microorganisms to public health. A common and serious form of contamination of aquifers is through leaks at gas stations (SMITH *et al*., 2003).

Thus, some residues can reach the soil and water bodies, part of them formed by aromatic hydrocarbons such as benzene, toluene and xylene (BTX), which can be highly toxic to the environment and to human health when they exceed the threshold value that the law requires. Due to the high toxicity of these compounds, it is necessary to improve the current techniques used on their removal.

Among the key technologies for the removal of these volatile organic compounds are those that destroy molecules, such as oxidation (WU *et al*., 2000) and biofiltration (NAMKOONG *et al*., 2003), and others which are used for removal and recovery of benzene as adsorption (STOFELA *et al*., 2015) or membrane separation (YEOW *et al*., 2003). Adsorption is notable for low cost and molecular selectivity, allowing separation of various components with low power consumption (SILVA *et al*., 2015).

Good adsorbent materials that are used in this process should have a high affinity for the compound to be removed and a wide variety of them have been applied in water treatment such as: clay (CANTUÁRIA *et al*., 2015), activated carbon (SABIO *et al*., 2006), red mud (SOUZA *et al*., 2011), organosilica (MOURA *et al*., 2011), among others.

Within the range of clay, organoclay are increasingly being employed to remove organic compounds. Despite the natural hydrophilic character of clay, you can turn it into a hydrophobic compound by the addition of organic molecules in the middle of its layers (PAIVA *et al*., 2008). Thus, their affinity for organic compounds is clear and becomes quite feasible to remove these pollutants.

In this context, this project has as main objective the study of the adsorption process in dynamic fixed bed system filled with organoclay Spectrogel type C for removal of benzene in aqueous solution.

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2. Materials and methods

According to previous study by Stofela *et al.* (2015), the commercial organoclay (Spectrogel type C) was sieved for 20 minutes to obtain 0.655 mm average particle size diameter (fraction between sieves of 24 and 28 Tyler mesh). This material was filled in a fixed bed of 6.5 cm in length and 0.65 cm in inner diameter and the tests were carried out with different flow rates (5, 10 and 20 mL.min^{-1}) of benzene in aqueous phase with 1.2 mmol.L^{-1} of initial concentration.

The solutions enter the fixed bed by a peristaltic pump and the container is subjected to agitation to keep it homogeneous. The benzene fluid enters at the bottom of the column and flows upward to avoid packing of the bed. The aliquots were analyzed by High Performance Liquid Chromatography (HPLC) with C18 column, mobile phase of 28% acetonitrile, 35% methanol and 37% of milli-Q water, with a wavelength of 206 nm to determine the concentration of the adsorbate.

To quantify this process, efficiency and mass transfer parameters were calculated for each breakthrough curve for each test. The adsorbate removal capacity was determined by the total amount removed (q_t) and by the useful amount removed until the breaking point (q_u) as expressed in Eq(1) and Eq(2), respectively.

$$q_t = \frac{C_0.Q}{m}\int_0^{\infty}\left(1-\frac{C}{C_0}\right)dt \tag{1}$$

$$q_u = \frac{C_0.Q}{m}\int_0^{t_r}\left(1-\frac{C}{C_0}\right)dt \tag{2}$$

Wherein C_0 is the initial concentration of adsorbate in solution (mmol.L^{-1}); Q is the flow rate (L.min^{-1}); m is the mass of adsorbent (g); C is the concentration of the adsorbate at time t; t_r is the breakthrough time (min).

Another important parameter is the height of mass transfer zone (MTZ) which is related to the effects of mass transfer. The MTZ moves evenly at a constant speed when the feed flow rate in the system is constant. The shorter the length of MTZ, the closer the system is from ideality, indicating greater removal efficiency (VIEIRA and SILVA, 2011). This parameter can be quantified by Eq(3), where h is the height of the bed (GEANKOPLIS, 1993).

$$h_{MTZ} = \left(1-\frac{q_u}{q_t}\right).h \tag{3}$$

Total Removal Percentage in the fixed bed (% Rem) is the adsorbate fraction retained in the adsorbent, considering all the solution used in the experiment. The %Rem can be calculated by Eq(4), where q_{in} is the total amount of adsorbate that entered the bed during the test.

$$\%Rem = \left(\frac{q_t.m}{q_{in}}\right).100 \tag{4}$$

Besides this parameter, the useful removal percentage in the bed can be determined (%Remu), it's analogous to the previous parameter, but only related to the amount removed until the bed breakthrough point. Eq(5) shows how to calculate the useful removal percentage in the bed.

$$\%Remu = \left(\frac{q_u.m}{q_{in}}\right).100 \tag{5}$$

Mathematical modeling was performed using the following models of Thomas (1944), Yan *et al.* (2001) and Clark (1987) using the software Maple 17. Eq(6) shows the Thomas model's equation to describe the bed behavior.

$$\frac{C}{C_0} = \frac{1}{1+\exp\left[K_T\left(\frac{q_T.m}{Q}-C_0.V\right)\right]} \tag{6}$$

Wherein K_T is the constant rate of adsorption (mL.mg^{-1}.min^{-1}), q_T is the maximum value of the solute concentration (mg.g^{-1}), V is the solution volume (mL) and m is the amount of adsorbent in column (g). To become easier the mathematical modeling the following considerations were assumed as Eq(7) and Eq(8) shows.

$$A_T = \frac{K_T.q_T.m}{Q} \tag{7}$$

$$B_T = K_T.C \tag{8}$$

The model developed by Yan *et al.* (2001) may be described by Eq(9).

$$\frac{C}{C_0} = 1-\frac{1}{1+\left(\frac{Q^2}{K_Y.q_Y.m}.t\right)^{K_Y.C_0/Q}} \tag{9}$$

Where Q_Y is the maximum adsorption capacity (mg.g^{-1}) and K_Y is the kinetic constant (L.min^{-1}.mg^{-1}). To facilitate mathematical modeling data, as in Thomas model, the following considerations were made (Eq(10) and Eq(11)).

$$A_Y = \frac{K_y.C}{Q} \tag{10}$$

$$B_Y = \frac{Q^2}{K_y q_y m} \tag{11}$$

Clark (1987) developed his model based on the concept of mass transfer associated with the Freundlich isotherm model, exposed by Eq(12).

$$\frac{C}{C_0} = \left[\frac{1}{1 + A_C.\exp(-r.t)}\right]^{1/_{n-1}} \tag{12}$$

Where n is the exponent of the Frendlich isotherm, A_c is the Clark constant and r is the mass transfer coefficient (min^{-1}).

Some parameters were used to evaluate the adjustment, like correlation of determination (R^2), adjusted correlation of determination (R^2adj), and Akaike Information Criterion (AIC) represented by Eq(13),Eq(14) and Eq(15), respectively, were applied.

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left({}^{C}/_{C_0}{}^{exp} - {}^{C}/_{C_0}{}^{calc}\right)^2}{\sum_{i=1}^{N}\left({}^{C}/_{C_0}{}^{exp} - \overline{{}^{C}/_{C_0}}\right)^2} \tag{13}$$

$$R^2{}_{adj} = 1 - \frac{N-1}{N-p}.(1 - R^2) \tag{14}$$

$$AIC = N.\ln\left[\sum_{i=1}^{N}\left({}^{C}/_{C_0}{}^{exp} - {}^{C}/_{C_0}{}^{calc}\right)^2\right] + 2.p \tag{15}$$

Where N is the number of data, ${}^{C}/_{C_0}{}^{exp}$ is the experimental value, ${}^{C}/_{C_0}{}^{calc}$ is the value calculated by the model, $\overline{{}^{C}/_{C_0}}$ is the average of the observed values and p is the number of adjustable parameters.

3. Results and discussion

The influence of feed flow was evaluated, maintaining initial concentration (1.2 mmol.L^{-1}) and bed height (about 2.0 g) constant. In order to obtain breakthrough curves, values of the ratio between of the tests in the fixed bed were plotted values of the ratio between the concentration of BTX in the effluent (C) and the concentration in the feed (C_0) as a function of time. Figure 1 compares the breakthrough curves for three benzene flow rates (5, 10 and 20 mL.min^{-1}) and Table 1 shows the experimental conditions and the parameters of efficiency and mass transfer obtained.

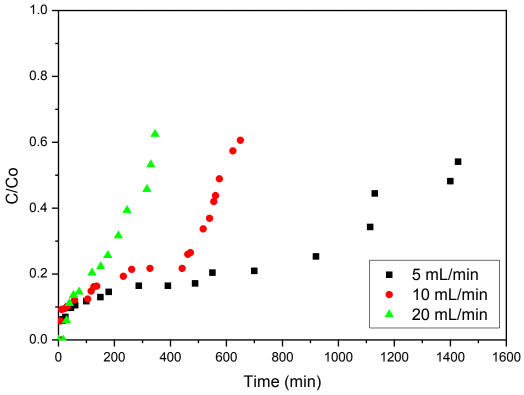


Figure 1: Effect of flow rate on column breakthrough curves for benzene adsorption.

Figure 1 shows an influence of the flow rate in the resistance to saturation because curves became more accentuated and reached faster saturation by increasing of the flow. The flow also influences the time required for the bed reach the equilibrium: the higher the flow, the less time is needed to saturate a column, as the column receives a higher adsorbate load, making active spots fill up faster, as expected. This behavior was also observed in the study with the organic compounds developed by Luz *et al*. (2013) and Brinques *et al*. (2005).

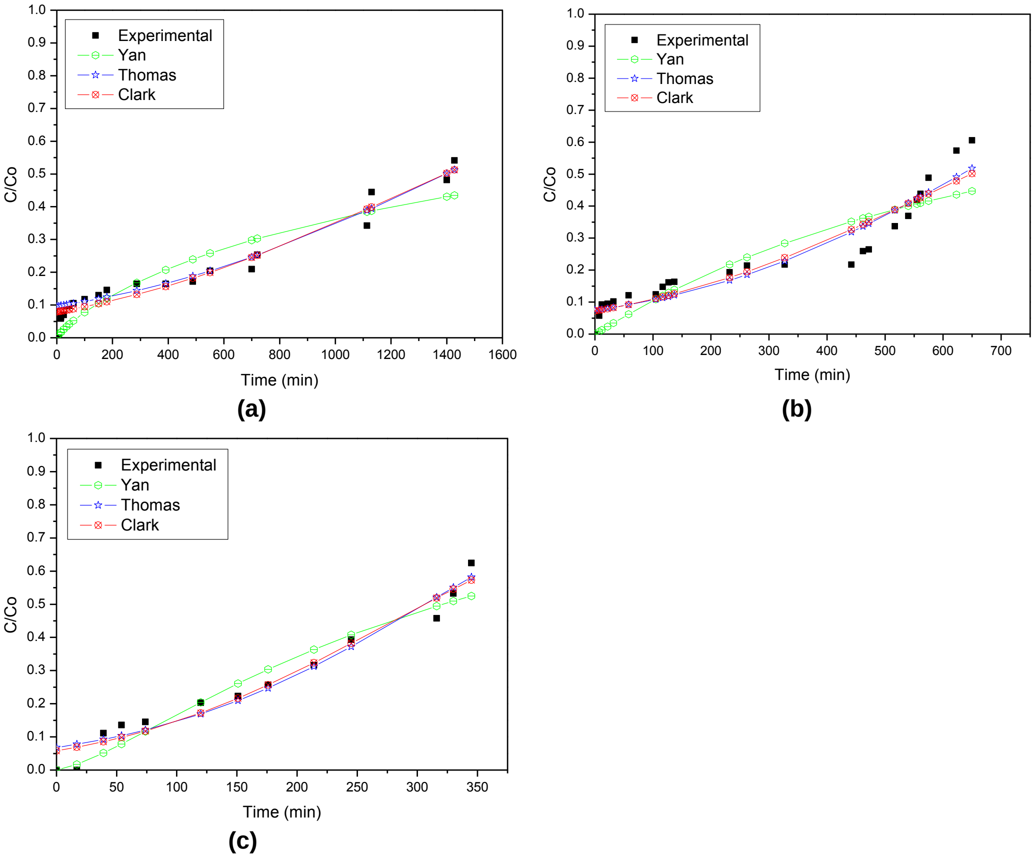
Table 1: Experimental conditions, efficiency and mass transfer parameters of benzene adsorption tests for the evaluation of flow rate effects

Flow rate (mL.min^{-1})	5	10	20
Breakthrough time (min)	14.446	7.448	28.743
Total time of tests (min)	1428	650	345
C/C$_0$ maximum	0.541	0.606	0.624
q$_t$ (mmol.g^{-1})	1.140	1.365	1.431
q$_u$ (mmol.g^{-1})	0.022	0.025	0.137
h$_{MTZ}$ (cm)	3.391	3.815	3.436
%Rem (%)	30.782	38.197	38.860
%Remu (%)	52.597	57.687	40.343

It can be observed that the test with a flow rate of 20 mL.min^{-1} shows the highest value for the height of the MTZ (h_{MTZ}), indicating that for high flow rates, the residence time of the adsorbate is not enough, disfavoring the process of adsorption. The lowest MTZ value was obtained for the test of 5 mL.min^{-1} and the value of the total amount of adsorbate removed (qt) was 1.140 mmol.g^{-1}. The total amount removed showed a decrease from 1.431 mg.g^{-1} to 1.140 mg.g^{-1} from the highest to the lowest investigated flow.

In a system where the equilibrium occurs with $C/C_0 = 1.0$, the value of the total amount of adsorbate removed is not influenced by the flow, because a variation in this parameter only affects a diffusion of the adsorbed in the liquid film and not in the solid material (KO *et al*., 2001). Once experimental data did not reach that value, the behavior was not followed. In relation to the percentages of removal, the useful percentage presented values higher than the total percentage of removal, indicating that the adsorption process occurred at a higher velocity at the beginning of the process when compared to the complete test.

The models of Thomas (1944), Yan *et al*. (2001) and Clark (1987) were fitted to breakthrough curves for modeling the experimental data and the results are shown in Figure 2. Values for the adjusted parameters are given in Table 2.



(a) (b) (c)

Figure 2: Experimental and predicted benzene breakthrough curves with flow rate of: (a) 5 mL.min^{-1}, (b) 10 mL.min^{-1}and (c) 20 mL.min^{-1} (initial adsorbate concentration = 1.2 mmol.L^{-1}).

Table 2: Effect of flow rate in Yan, Thomas and Clark model parameters for benzene breakthrough curves.

5 mL.min^{-1}							
					R²	R²adj	AIC
YAN	A_Y (10^3.mL^{-1}) 0,8293	B_Y (10^{-3}.mL.min^{-1}) 0,0005	q_Y (mg.g^{-1}) 1,3701	k_Y (L.mg^{-1}.min^{-1}) 14,7459	0,8764	0,7545	-50,338
THOMAS	A_T 2,3239	B_T (mg^{-1}) 0,0017	q_T (mg.g^{-1}) 0,9563	k_T (mL.mg^{-1}.min^{-1}) 6,0456	0,9697	0,9369	-80,790
CLARK	A_C 2,1342	r (min^{-1}) 0,0012	-	-	0,9685	0,9343	-79,938
10 mL.min^{-1}							
					R²	R²adj	AIC
YAN	A_Y (10^3.mL^{-1}) 1,0363	B_Y (10^{-3}.mL.min^{-1}) 0,0013	q_Y (mg.g^{-1}) 1,1584	k_Y (L.mg^{-1}.min^{-1}) 36,8529	0,8158	0,6489	-42,038
THOMAS	A_T 2,5138	B_T (mg^{-1}) 0,0039	q_T (mg.g^{-1}) 0,9179	k_T (mL.mg^{-1}.min^{-1}) 14,1254	0,9084	0,8164	-60,971
CLARK	A_C 2,3634	r (min^{-1}) 0,0028	-	-	0,8925	0,7863	-57,726
20 mL.min^{-1}							
					R²	R²adj	AIC
YAN	A_Y (10^3.mL^{-1}) 1,3821	B_Y (10^{-3}.mL.min^{-1}) 0,0031	q_Y (mg.g^{-1}) 0,8986	k_Y (L.mg^{-1}.min^{-1}) 98,3029	0,9493	0,8929	-46,864
THOMAS	A_T 2,6182	B_T (mg^{-1}) 0,0085	q_T (mg.g^{-1}) 0,8576	k_T (mL.mg^{-1}.min^{-1}) 30,3953	0,9550	0,9047	-49,841
CLARK	A_C 2,7113	r (min^{-1}) 0,0064	-	-	0,9602	0,9155	-51,419

It was observed that the value found for the parameter q_T of the Thomas model and q_Y for the Yan model in the three flows investigated did not follow the same trend as the values obtained experimentally, that is, an increase in the feed rate caused a decrease in the total amount adsorbed. However, the values obtained by the model in the three flows investigated were smaller than the experimental qt, with the exception of the Yan model in the test with the lowest flow rate.

The kinetic coefficients k_Y and k_T were shown to be proportional to the increase in feed rate once there is a decrease is due to the decrease in the resistance of the liquid film interface (KO *et al*., 2001).

The best adjustments were obtained by the Thomas model for smaller flows, however for the maximum flow (20 mL.min^{-1}), the best fit was provided by the Clark model. Probably differences in Thomas and Clark models are so small that cannot be seen due to uncertainties in measurements. This system is shown by Stofela *et al*. (2016) as being of pseudo-second order and, given that the Thomas model was developed for these systems, this good prediction was expected. Despite this, it can be verified that for high flow rates the model cannot predict properly the behavior.

The values obtained for the error analysis parameters shows that all models have a good prediction of the liquid phase benzene adsorption with organophilic clay. High values of R² and R²adj together with low values of AIC show that all three models tested are able to describe this adsorption process.

4. Conclusions

With the fluid dynamics study, it was possible to evaluate efficiency parameters. Thus, it was verified that the flow rate of 5 mL.min^{-1} provided the best results for the removal of benzene within the studied range because it presented the lowest MTZ height value (3,391 cm) with removal of 1.140 mg.g^{-1} of benzene.

The models of Thomas, Yan and Clark were adjusted to the breakthrough curves, presenting satisfactory results with maximum R²adj values of up to 0.9697 for the Thomas model. As the system is of a pseudo-second order type and this model has this characteristic as a premise, it was expected to obtain a good fit to the tests, but for high flow rates the Clark model fit better.

It can be concluded that the organophilic clay Spectrogel that was applied in this study could be well used in fixed bed system at low flow rates, with promising results for application in treatments of aqueous effluents contaminated with benzene through adsorption.

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