ADSORPTION OF TOLUENE FROM AQUEOUS SOLUTION ONTO A GRANULAR ACTIVATED CARBON BED IN A PILOT PLANT

Graziela Brusch Brinques[*], Talita Furlanetto Mendes, Keiko Wada, M. P. M. P. Cardozo

Departamento de Engenharia Química - Universidade Federal do Rio Grande do Sul

Abstract. The adsorption in fixed bed of activated carbon is one the most important alternatives to the removal of volatile organic compounds (VOC´s) in aqueous effluents at low concentrations. The objective of this work is the development of a methodology to evaluate the performance of adsorbents in a pilot plant to be used in the design of fixed bed adsorption units. It was carried out experiments, at ambient temperature, for acquisition of the breakthrough curves in the adsorption of toluene from an aqueous stream, in a fixed bed of granular activated carbon. The experiments were performed in a pilot plant that is provided with jacketed column with 20 mm of inner diameter. The fixed bed was formed by a previously prepared commercial activated carbon (8 x 12 mesh). Different depths of bed and flow rates were tested, keeping the feed concentration around 50 ppm. This unit is equipped with an on-line UV detector, allowing the measurement of the VOC in the effluent stream. It, also, has modules for the acquisition of temperature, flow rate and differential pressure data. Concomitantly, it was carried out tests to characterize the solid adsorbent, such as ash and moisture contents, density, porosity and surface area and to obtain parameters needed in the modeling of the adsorption process. The estimation of the mass diffusivity and the mass transfer coefficient in the solid phase were done through kinetic test data. The developed methodology can be applied in future studies of removal of other contaminants with different adsorbents.

Keywords: Adsorption, Granular Activated Carbon and Toluene.

1. Introduction

There are a large number of commercial adsorbents, among these are traditional adsorbent as silica gel, activated alumina and activated carbon, as well as new developments of zeolite and resins. Adsorption on activated carbon is one of the most effective and safety technology currently available for the treatment of drink water and wastewater contaminated with low concentrations of hazards compounds (Chatzopoulos et al., 1993; Li et al., 2002). The use of granular activated carbon beds in tertiary treatment procedure would appear to be a more viable alternative because of the superior recovery and regeneration properties of carbon in the granular form (Martin and Iwugo, 1982). Various authors have been studied the adsorption onto granular activated carbon (Hindarso et al. 2001; Chern and Chien, 2002). Among these contaminants, there is the group of volatile organic compounds (VOC´s), within toluene is included. It is important material in the chemical industry as a raw material in chemical manufacture, and it is usually used as solvent in a wide variety of manufacturing processes.

Important steps in the study of adsorption separation process are the analysis of the solid-liquid equilibrium data and the adsorbent characterization. There are few data about adsorption of toluene from aqueous solutions onto granular activated carbon.

The fixed-bed adsorption is a transient process, and for which it can be obtained the breakthrough curve that gives the adsorbate concentration in the effluent along the time. Due to this fact and the information lack for many different configuration systems, several authors have been studied the breakthrough curves (Wolborska and Pustelnik, 1996; Chern and Chien, 2001, 2002). Many factors can influence on the adsorption operation in fixed bed, among these are the bed temperature, feed concentration, flow rate, bed depth and adsorbent type.

The objective of this work is the development of a methodology to evaluate the performance of adsorbents in a pilot plant to be used in the design of fixed bed adsorption units. Concomitantly, it were carried out tests to obtain adsorption isotherm data, kinetic data and the characterization of adsorbent.

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[*]Graziela Brusch Brinques.
Address: DEQUI – UFRGS. Rua Prof. Luiz Englert, S/N°, Campus Central, CEP: 90040-040, Porto Alegre, RS, Brazil
E-mail: grazibb@enq.ufrgs.br

2. Methods

2.1. Carbon Characterization

A commercial granular activated carbon (8 x 12 mesh) was chosen as adsorbent. In this study, the solid adsorbent was characterized by the determination of ash and moisture contents, pH, bulk and real density and surface area. The ash content (% ash) was determined through the weight loss of approximately 5 g of granular activated carbon placed into weighted ceramic crucibles. The samples were heated in a muffle furnace at 650 ºC for at least 10 h. The crucibles were cooled in a desiccator and residual solids (ash) were weighed. The ash content was calculated by the Eq. (1):

$$\% \, ash = \frac{residual \; solid \; mass \; (g)}{initial \; \, carbon \, mass \; (g)} \times 100 \tag{1}$$

The moisture content was determined by the weight loss of 5 to 10 g of samples that were weighted and placed into weighed recipients. The samples were heated in a furnace at 150 ºC for at least 3 h. The recipients were cooled in a desiccator, and dried carbon samples were weighted. The moisture content was calculated by the Eq. (2):

$$\% \; moisture = \frac{initial \; carbon \; mass \, (g) - final \; carbon \; \, mass \, (g)}{initial \; carbon \; mass \, (g)} \times 100 \tag{2}$$

The pH was determined using a 1% (wt./wt.) suspension of activated carbon on de-ionized water. The suspension was heated to approximately 90 ºC and stirred for 20 min. Then, the suspension was allowed to cool until the room temperature and the pH was measured with a pH meter (Ingold, pH-206, with AgCl electrode). The pH meter was initially calibrated with pH 4 and pH 7 buffers.

The bulk density (ρ_B) was determined using 100 mL graduated tube that was filled with 8x12 mesh granular activated carbon. The filled tube was weighed and the bulk density was calculated by the Eq. (3):

$$\rho_{\mathbf{B}} = \frac{weight \; of \; activated \; carbon \; (g)}{volume \; of \; activated \; carbon \; bed \; (mL)} \tag{3}$$

The real density (ρ_r) was determined using approximately 2 g of activated carbon. The weighted activated carbon was placed in a flask and it was filled with water. The set was heated to approximately 100 ºC to eliminate the air in the pores. After the sedimentation of carbon, the suspension was allowed to cool to room temperature and the activated carbon was transferred to a 100 mL volumetric flask. This flask was then filled with water. The set was weighed and the volume of water was calculated using the water density at room temperature and the real density was calculated by Eq. (4)

$$\rho_{\mathbf{B}} = \frac{weight \; of \; activated \; carbon \; (g)}{volume \; of \; activated \; carbon \; (mL)} \tag{4}$$

The internal surface area of pores was measured by nitrogen adsorption at 77 K, using the BET equation. It was used a Quantachrome analyzer (Quantachrome Corporation, model MP).

2.2. Pretreatment of the granular activated carbon

Approximately 100 g of granular activated carbon (8 x 12 mesh) were washed with approximately 200 mL of distilled and de-ionized water at boiling temperature for 30 min. This procedure was repeated 10 times. In each step of washing, the activated carbon was filtrated in sintered glass filter. Finally, the activated carbon was dried at 105 ºC, then it was cooled in a desiccator and stored in closed flasks.

2.3. Feed solution preparation and chemical analysis

Toluene (Quimex, 99.5%, PA-ACS; Synth, 99.5 %, PA-ACS) was used as solute. Its density is in the range of 0.865-0.869 $g.L^{-1}$ at 20 ºC. All toluene solutions were prepared with distilled and de-ionized water. The toluene concentrations in the aqueous solution were measured using a spectrophotometer UV – Visible (CARRY 300, VARIAN) at 254 nm and 100 mm optical path. Two calibration curves were elaborated, one to be used with those solutions that were not previously membrane filtered, before the analysis on spectrophotometer, and the other to be used with the solutions that were previously membrane filtered before the analysis on spectrophotometer (in the case of kinetic tests solutions).

2.4. Kinetic test

The kinetic tests for toluene adsorption from an aqueous solution onto granular activated carbon (8 x 12 mesh) were done at 25 ± 1 ºC. This experiments were carried out by adding a known mass of activated carbon (1 or 2 g) to a series of 250 mL glass-stopped flasks filled with 250 mL of 100 ppm toluene solution. The glass-stopped flasks were then placed in a thermostatic shaker bath (DUBNOFF, TE-053) for 24 h. A blank flask, in the absence of activated carbon, was included in each batch and it was used to determine the initial concentration in the flasks in the batch. At determined intervals periods, a sample from each flask was taken with a glass syringe, filtered through membrane filters (MILLEX LCR, modified membrane PTFE, 0,45 μm e 25 mm, MILLIPORE) and analyzed. The cell of spectrophotometer analyzer was dried to avoid dilution effects. After measuring, the samples were then returned to the flask. This procedure was repeated until the solution absorbance value was constant.

The solute concentration on the activated carbon, q $(mg.g^{-1})$, was calculated from the initial solute concentration in liquid-phase and its concentration at each sample by the Eq. (5).

$$q = \frac{(c_0 - c)V}{m} \tag{5}$$

where c_0 is the initial solute concentration $(mg.L^{-1})$, c is its concentration at each sample $(mg.L^{-1})$, V is the volume of solution (L), and m is the mass of activated carbon (g).

The mass diffusivity coefficient (D_s) for 1 and 2 g of activated carbon were estimated through Eq. (6).

$$\frac{\overline{q}}{q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-D_s n^2 \pi^2 t}{R^2}\right) \tag{6}$$

where D_s is the mass diffusivity coefficient $(m^2.h^{-1})$, R is the medium radius of adsorbent particle (m), t is the time (h), n is the number of terms of the sum, $\overline{q}$ is the mean concentration of solute in the adsorbent $(mg.g^{-1})$ and q_∞ is the solute concentration in the adsorbent at infinite time $(mg.g^{-1})$. Using the D_s value and considering an spherical particle, it is possible to calculate the solid-phase mass transfer coefficient, k_s ($m.h^{-1}$) by Eq. (7):

$$k_s = \frac{5 D_s}{R} \tag{7}$$

2.5. Breakthrough curves

The breakthrough curves were obtained in a pilot plant, whose schematic diagram is shown in Figure 1. This plant has a jacketed glass column with 20 mm of inner diameter and the experiments were carried out at 25 ºC. The fixed bed was formed by a previously prepared commercial activated carbon (8 x 12 mesh).Two bed depths (5 and 10 cm) and two flow rates (0,8 and 1,6 $L.h^{-1}$) were tested, and the feed concentration was kept around 50-60 ppm. This unit is equipped with on-line UV detector, allowing the measurement of the VOC in the effluent stream. It, also, has modules for the acquisition of temperature, flow rate and differential pressure data. The Elipse software was used to configure the interface for data acquisition and command systems and to data registration it was used the database of Access Windows.
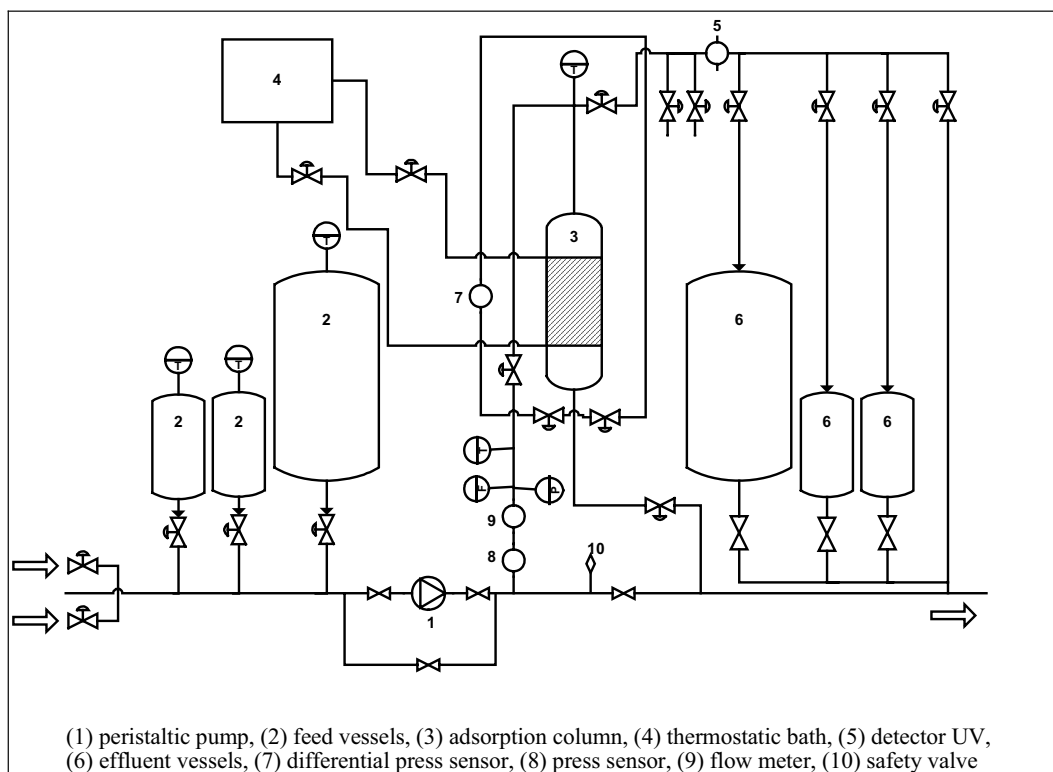
(1) peristaltic pump, (2) feed vessels, (3) adsorption column, (4) thermostatic bath, (5) detector UV,
(6) effluent vessels, (7) differential press sensor, (8) press sensor, (9) flow meter, (10) safety valve

Fig. 1. Schematic diagram of the fixed-bed adsorption pilot plant.

3. Results and Discussions

The results of the analysis of granular activated carbon are given in Table 1. The parameters values estimated from experimental kinetic tests with 1 and 2 g are shown in Table 2. In these tests, the initial concentration of the toluene aqueous solution was 108 ppm. It can be seen that the estimated values are fairly close, suggesting the use of a mean value. The mean values for mass diffusivity and solid-phase mass transfer coefficient were 6,1 $cm^2.h^{-1}$ and 0,0162 $cm.h^{-1}$, respectively. The D_s value is in agreement with Chatzoupoulos, Varna, Irvine (1993).

The experimental conditions for the fixed bed runs are shown in Table 3. It can be observed, that for each run, the concentration of feeding solution have presented oscillations, partially due to toluene loss by volatilization. To minimize this loss during the experiments, it was used a floating polyethylene cover and it was, also, made several tank refilling to avoid wide level variation of feed solution tank. However, even with these arrangements oscillations happened.

Table 1. Data from carbon characterization.

Physics and Chemical Properties	Value
Surface area	681 $m^2.g^{-1}$
Moisture content.	15.4 %
Ash content	8.7 %
Bulk Density	0.50 $g.mL^{-1}$
Real density	1,72 $g.mL^{-1}$
Sieve fraction	8 x 12 mesh
Particle mean diameter	1.895 mm
pH of carbon suspension	8.3
Mean pore diameter	23.7 Å

Table 2. Estimated values for D_s and k_s.

	Kinetic test with 1 g of carbon	Kinetic test with 2 g of carbon
D_s (cm^2.h^{-1})	6.5 x10^{-4}	5.7 x10^{-4}
k_s (cm.h^{-1})	0.0172	0.0151

Table 3. Experimental Conditions for fixed bed runs.

Test	Bed depth (cm)	Flow rate (L.h^{-1})	Carbon mass (g)	Solute initial concentration, c_0 (ppm)	Final breakthrough time (h)
Run 1	10	0.8	20.3888	49 ± 5	229.2
Run 2	10	0.8	20.0005	62 ± 7	197.5
Run 3	5	0.8	10.0007	60 ± 1	110.2
Run 4	5	0.8	10.0016	64 ± 3	107.7
Run 5	10	1.6	20.0008	55 ± 4	117.7
Run 6	10	1.6	20.0010	52 ± 4	117.6
Run 7	5	1.6	10.0017	55 ± 3	68.8
Run 8	5	1.6	10.1793	65 ± 2	77.4

In Figure 2, it is presented the toluene concentration on the effluent along time in several fixed-bed runs. It can be observed that toluene concentration was close to zero, on the initial part of the curves, and it was increased with the increasing of operation time, but it was not reached a constant value. For this reason, the final breakthrough time was defined here, as the time in which the toluene concentration at the effluent didn't increase significantly. The final breakthrough time are presented in Table 3. Besides that, toluene concentration in the effluent did not reach the same concentration of the feed solution. In Chatzoupoulos and Varna (1995) experiments of toluene adsorption on fixed bed, similar fact was reported.

In Figures 3 and 4, it is shown some breakthrough curves where the influence of the flow rate on the adsorption, for the same bed depth, can be compared. It is possible to verify that, for the same bed depth, to the higher flow rate corresponds the smaller time to reach bed saturation. In Figures 5 and 6, it is shown some breakthrough curves where the influence of the bed depth on the adsorption for the same flow rate can be compared. It is possible to verify that, for the same flow rate, to the higher bed depth corresponds the larger time need to reach bed saturation. These observations are in agreement with Chern and Chien (2001, 2002).

Regarding the form of the curves in Figure 5, it is possible to observe that they are fairly distinct. If it is made a superposition of the curves of experiments with the same flow rate and distinct depths, it is not possible to overlap these curves, this is an indication that it was developed a proportional pattern behavior.
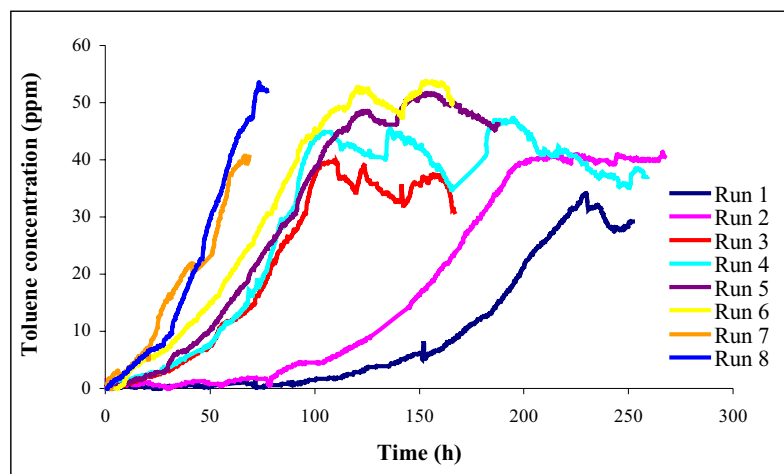

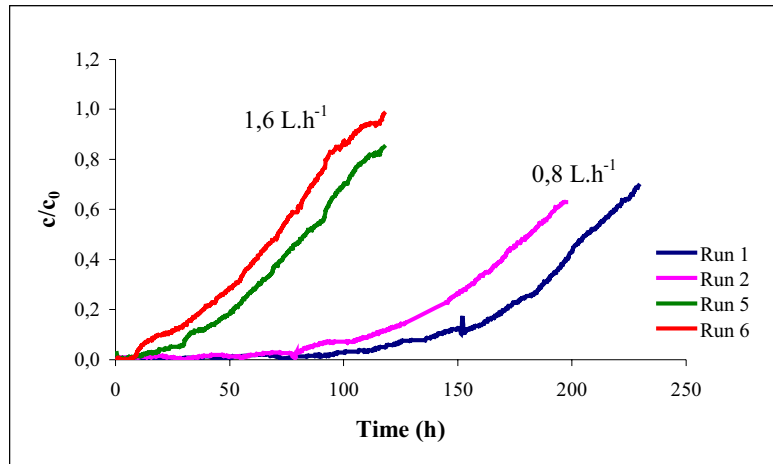**Fig 2.** Toluene concentration on the effluent vs. operation time.

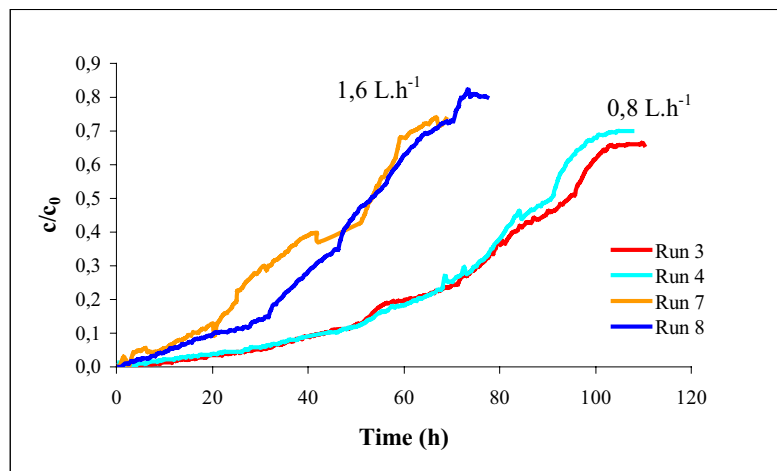**Fig 3.** Breakthrough curves for twoflow rates and bed depth of 10 cm.

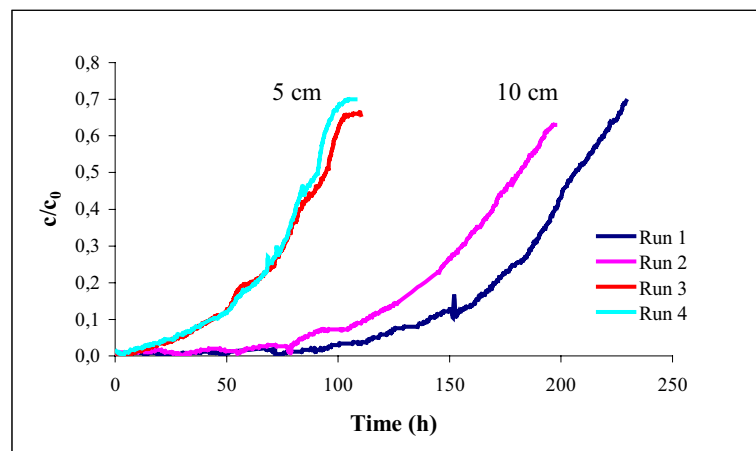**Fig 4.** Breakthrough curves for two flow rates and bed depth of 5 cm.

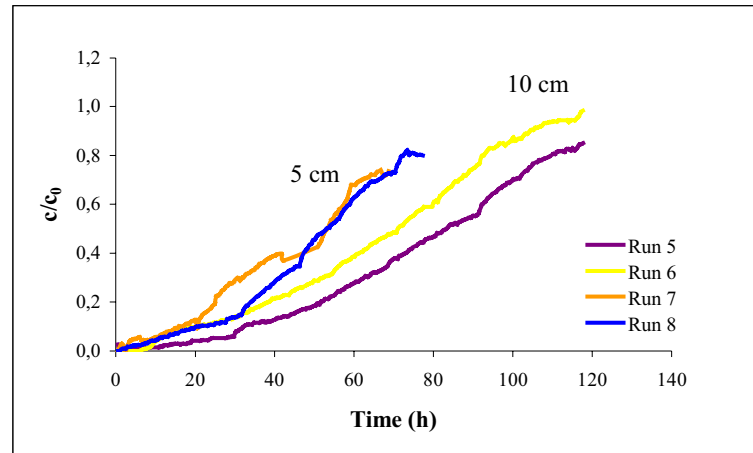**Fig 5.** Breakthrough curves for two bed depths and flow rate of 0.8 L.h^{-1}.

Fig 6. Breakthrough curves for two bed depths and flow rate of 1.6 L.h^{-1}.

For each fixed bed adsorption run, the mass zone transfer depth (MZTL) and the mass of toluene adsorbed are estimated. These values are given in Table 4. Analyzing the values corresponding to the runs with flow rate of 0.8 L.h^{-1} and with different bed depth, it possible to verify that the MZTL increased with the increasing of the bed depth. This fact could be due to greater spreading of the adsorption fronts in the experiments with the longer bed. In such case, to project a industrial adsorver based on experimental data, the pilot plant bed must have the same depth of industrial bed and it must be operated at the same superficial velocity. For the runs with flow rate of 1.6 L.h^{-1} and different bed depths, the MZTL were too close to the total depth of the bed and so larger bed depths should be investigated.

Table 4. Estimated values of MZTL and mass of toluene retained on fixed bed runs.

Test	Bed depth (cm)	Flow rate (L.h^{-1})	MZTL (cm)	Mass of toluene detained (g)
Run 1	10	0.8	6.7	7.7
Run 2	10	0.8	6.3	8.3
Run 3	5	0.8	4.2	4.1
Run 4	5	0.8	4.4	4.2
Run 5	10	1.6	8.5	7.0
Run 6	10	1.6	8.7	5.6
Run 7	5	1.6	4.7	4.1
Run 8	5	1.6	4.6	5.4

The 5 cm bed depth seemed, also, to be too short for both flow rates investigated, since the MZTL were close to the total depth of the bed. However, when the experiments with the 10 cm bed were analyzed, it was observed that the MZTL were distinct.

For the estimation of the liquid-phase mass transfer coefficient, it was used the Wilson and Geankoplis correlation (COONEY, 1999) presented in Eq. (8).

$$j_D = \frac{1.09}{\varepsilon} Re^{-2/3} \tag{8}$$

where j_D is the Colburn factor, which is defined by $(k_f/\varepsilon v)(Sc)^{2/3}$, where Sc is the Schmidt number, that is equal to $\mu/\rho.D_{AB}$, Re is the Reynolds number and ε is bed porosity. The estimated values were 5.4 x.10^{-6} and 6.81x10^{-6} m.s^{-1} for the experiments with flow rates of 0.8 and 1.6 L.h^{-1}, respectively. With this values and the k_s value of kinetc test with 1 g of carbon, it was calculated the resistence in the 2 phases (Table 5). When the 2 resistances were compared, it is possible to note that the mass transfer resistance in the liquid phase is negligible when it is compared with the mass transfer resistence in solid phase.

7

Table 5. Estimated values of mass transfer resistance in the liquid and solid phase.

Flow rate (L.h^{-1})	Mass transfer resistance in the liquid phase (s.m^{-1})	Mass transfer resistance in the solid phase (s.m^{-1})
0.8	1.85 x10^5	2.09x10^7
1.6	1.47 x10^5	

4. Conclusions

The experimental work at the pilot plant has demonstrated that it is adequate to develop adsorption studies in fixed bed, allowing for the long test runs needed. However, when it is working with volatile compounds as toluene special care should be taken to avoid solute losses.

The mass transfer zones length values for the pair solute/adsorbent employed were very close to bed depths, so larger bed depths should be investigated.

The mean value for mass diffusivity in the solid was $6.1x10^{-4}cm^2.h^{-1}$ and it is in agreement with literature data.

The mass transfer resistence in the liquid phase could be negligible, when the values of the mass transfer resistance in both phases were compared.

References

Benkhedda, J., Jaubert, J.N., Barth, D. (2000). Experimental and Modeled Results Describing the Adsorption of Toluene onto Activated Carbon. Journal of Chemical and Engineering Data, 45, 650.

Chatzopoulos, D., Varma, A. (1995). Aqueous-phase Adsorption and Desorption of Toluene in Activated Carbon Fixed Beds: Experiments and Model. Chemical Engineering Science, 50,127.

Chatzopoulos, D., Varma, A., Irvine; R.L. (1993) Activated Carbon Adsorption and Desorption of Toluene in the Aqueous Phase. AIChE Journal, 39, 2027.

Chern, J.M., Chien, Y.W. (2001) Adsorption Isotherm of Benzoic Acid onto Activated Carbon and Breakthrough Curves in Fixed-Bed Columns. Industrial & Engineering Chemistry Research, 40, 3775.

Chern, J.M., Chien, Y.W. (2002) Adsorption of Nitrophenol onto Activated Carbon: Isotherms and Breakthrough Curves. Water Research, 36, 647.

Hindarso, H., Ismadji, S., Wicaksana, F., Mudjijati, Indraswati, N. (2001). Adsorption of Benzene and Toluene from Aqueous Solution onto Granular Activated Carbon. Journal of Chemical and Engineering Data, 46, 788.

Li, L.,Quinlivan, P.A., Knappe, D.R.U. (2002). Effects of Activated Carbon Surface Chemistry and Pore Structure on the Adsorption of Organic Contaminants from Aqueous Solution. Carbon, 40, 2085.

Martin, R. J., Iwugo; K. O. (1982).The Effects of pH and Suspended Solids in the Removal of Organics from Waters and Wastewaters by the Activated Carbon Adsorption Process. Water Research, 16, 73.

Pires, J., Pinto, M., Carvalho, A., Carvalho, M.B. (2003). Adsorption of Acetone, Methyl Ethyl Ketone, 1,1,1-trichloroethane, and Trichloroethylene in Granular Activated Carbons. . Journal of Chemical and Engineering Data, 48, 416.

Wolborska, A., Pustelnik, P.A. (1996). A Simplified Method for Determination of the Break-through Time of an Adsorbent Layer. Water Research, 30, 2643.