REVISTA DE CIÊNCIAS AMBIENTAIS - RCA (ISSN 1981-8858)

http://revistas.unilasalle.edu.br/index.php/Rbca

Canoas, v. 14, n. 2, 2020

http://dx.doi.org/10.18316/rca.v14i.4366

KINETIC STUDY ON THE REMOVAL OF BTX COMPOUNDS IN BATCH REACTOR USING ACTIVATED CARBON FROM COCONUT SHELL AS THE ADSORBENT

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ABSTRACT

The adsorption kinetics of BTX compounds (benzene, toluene, o-xylene) in aqueous solution was investigated in a batch reactor at 23 ±1°C using a commercial thermally-activated coconut shell carbon. The solution pH did not affect the adsorption and the thermal activation of the adsorbent produced a higher amount of negative charges on the surface, increasing the adsorption efficiency, due to the weakly positive charges of the BTX molecules. In order to determine the mechanism and the limiting step of the adsorption process, the kinetics data were fitted using different models: the pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The pseudo-second-order model was more appropriate for describing the adsorption rate based on the high correlation coefficient (R^2) and because the q_e calculated was reasonably similar to q_e experimental values. Through a detailed study involving kinetic experiments it was also possible to identify the controlling stage of the process from the fitting of the intraparticle diffusion model. The high values for the correlation coefficients indicated that the process is strongly controlled by the second-stage of the diffusion for all compounds studied at different concentrations.

Keywords: BTX; Adsorption Kinetics; Pseudo-First-Order; Pseudo-Second-Order; Intraparticle Diffusion.

RESUMO

Estudo cinético da remoção dos compostos BTX em reator batelada usando carvão ativado de casca de coco como adsorvente. A cinética de adsorção dos compostos BTX (benzeno, tolueno, o-xileno) em solução aquosa foi investigada em um reator em batelada a 23 ±1°C usando carvão de casca de coco ativado termicamente comercial, como adsorvente. O pH da solução não afetou a adsorção e a ativação térmica do adsorvente produziu uma maior quantidade de cargas negativas na superfície, aumentando a eficiência de adsorção, devido às cargas das moléculas dos BTX serem fracamente positivas. Para determinar o mecanismo e a etapa limitante do processo de adsorção, os dados cinéticos foram ajustados usando diferentes modelos: modelos de pseudo-primeira ordem, pseudo-segunda ordem e difusão intrapartícula. O modelo de pseudo-segunda ordem foi o mais apropriado para descrever a taxa de adsorção com base no alto coeficiente de correlação (R^2) e porque o q_e calculado utilizando o modelo de pseudo-segunda ordem foi razoavelmente

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semelhante aos valores experimentais. Através de um estudo detalhado envolvendo os experimentos cinéticos, também foi possível identificar o estágio controlador do processo a partir do ajuste do modelo de difusão intrapartícula. Os valores elevados para os coeficientes de correlação indicaram que o processo é fortemente controlado pelo segundo estágio da difusão para todos os compostos estudados em diferentes concentrações.

Palavras-Chave: BTX; Cinética De Adsorção; Pseudo-Primeira Ordem; Pseudo-Segunda Ordem; Difusão Intrapartícula.

INTRODUCTION

Benzene, toluene and xylenes (BTX) are organic compounds that are frequently present in chemical and petrochemical effluents. Because of their strong toxicity to humans and marine life, stringent regulations have been imposed on the concentration levels of these compounds in effluents for safe discharge (Luz et al., 2013; Luz et al., 2018; Anjum et al., 2019). These compounds are designated by the USEPA (United States Environmental Protection Agency) as priority chemicals that need to be reduced to low levels in effluents prior to discharge (Lin and Huang, 1999; Guelli U. de Souza et al., 2012).

Various conventional and advanced technologies have been used to treat and remediate effluents that are contaminated with BTX and to reduce the costs of current treatments (Haddad et al., 2015) The technologies that are widely applied for the removal of organic compounds generally include biological treatments, membrane filtration and adsorption onto synthetic zeolites or onto activated carbon (Vidal et al., 2011; Vidal et al., 2012; Haddad et al., 2015; Anjum et al., 2019). According to Chatzopoulos et al. (1993) and Wibowo et al. (2007), activated carbon is a proven and reliable technology for the industrial removal of small quantities of organic compounds which are soluble in water and industrial effluents.

In this context, the aim of this study was to investigate the removal of BTX compounds in aqueous solution in a batch reactor at 23 ± 1°C using thermally-activated coconut shell carbon. In order to evaluate the influence of the concentration on the removal of BTX compounds four different initial concentrations of the contaminants were evaluated. Subsequently, a kinetic study of the BTX compounds was carried out to determine the most appropriate model to describe the adsorption process in question. In this study, the pseudo-first order and pseudo-second order kinetic models were investigated, and the intraparticle diffusion model was evaluated to figure out the controlling step of the BTX adsorption.

MATERIALS AND METHODS

The adsorbent used was carbon from coconut shell, produced by Carbomafra industry, located in Curitiba – Brazil, which it was thermally activated with vapor and carbon dioxide in the temperature range of 800-1000 °C (Carbomafra, 2006). The solvents used were distilled water to prepare the solutions of BTX compounds, benzene standard (HPLC grade; Fluka), toluene standard (UV spectroscopy/HPLC grade; VETEC), and 98% o-xylene standard (HPLC grade; SigmaAldrich). For the high performance liquid chromatography (HPLC), MilliQ water and methanol standard (HPLC grade; Carlo Erba Series Gold) were used.

Experimental Procedure

Before the laboratory tests, the samples passed through a pretreatment which consisted of adjusting the granulometry to approximately 0.85 mm (obtained from preliminary tests). The determination of particle size was done by conducting granulometric analysis, placing 100 g or 200 g of activated carbon in sieves with standard mesh, which are mechanically agitated for at least 15 min (sieve agitator of the MinorEndecotts brand). The activated carbon retained in each sieve was separated and stored. In order to determine the concentration of BTX compounds a high performance liquid chromatography (HPLC) gas chromatograph (GC) connected to a UV/vis detector (model CG 437-B) and a Nucleosil C18 reverse-phase column of 250 mm, with an internal diameter of 4.6 mm, were used. The mobile phase employed in the HPLC, composed of methanol and Milli-Q water (80:20), was used at a flow rate of 0.8 mL/min. The BTX compounds were identified at a wavelength of 254 nm. All the experiments were carried out in triplicate, adopting an average error of less than 5%.

Characterization of Adsorbent

The characterization of the adsorbent was based on the following tests: particle size, hardness and moisture, volatile matter, ash and fixed carbon contents (Carbomafra, 2006; ABNT, 1989). We also performed experiments for the determination of the surface functional groups of the activated carbon (Boehm, 1994). The B.E.T. (Brunauer, Emmett and Teller) and B.J.H. (Barrett, Joyner and Halenda) tests were carried out in order to determine the surface area and pore volume, size and distribution, as well as the particle irregularity of the material. B.E.T. adsorption isotherm was used to calculate the surface area of the microporous adsorbents. Created in 1938 by Brunauer, Emmett and Teller, the method is based on the determination of the volume of nitrogen adsorbed at various pressures, at the temperature of liquid nitrogen, employed in the equation deduced by them, allowing the determination of the volume of nitrogen necessary to form a monomolecular layer over the adsorbed material (Brunauer et al., 1938). To do so, the volume of the monolayer is obtained by the volume of gas adsorbed at a certain pressure. To conduct the adsorption trial, approximately 100 mg of the sample of activated carbon were weighed and placed in a quartz crystal cell, in which the samples were prepared to remove the residual moisture and remaining volatiles present. To do that, the samples underwent a degassing process in a gas station of the equipment, in which they remained for 20 hours, at 200ºC, and under 0.1 mmHg vacuum. After this treatment, the sample was conditioned in an analysis station, where it remained immersed in liquid nitrogen during all the trials to maintain thermal stability. The B.J.H. method uses the Kelvin equation and it assumes the progressive emptying of the pores filled with liquid, with the decrease in pressure. It can be applied for both adsorption and desorption, since the decrease in pressure begins where the pores are considered completely full, normally for P/P0 equal to 0.95, or at a pressure of 95% of saturation. The equipment used for the BET and BJH analyzes was the QUANTA CHROME surface area and pore size analyzer; Model Nova 1200e. B.E.T. and BJH were held at the Institute of Engineering and Technology of the University of the Extreme South of Santa Catarina – UNESC. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDAX) were carried out to obtain micrographs of the physical structure and determine some of the chemical elements contained in the sample. The microscopic images and the elemental composition of the samples were obtained using the Philips Scanning Electron Microscope, model XL 30 with tungsten filament, equipped with EDAX (X-ray Dispersive Energy Spectroscopy) from the UFSC Microstructural Characterization (LCM) Laboratory. The samples were covered with gold using the BAL-TEC Sputter Coatter SCD 005 device. The magnifications of the micrographs are 30 and 125 times.

Effect of pH

To study the effect of pH on the activated carbon adsorption, the experiments were carried out at an initial BTX concentration of 150 mg/L. The adsorbent mass used in the experiment was 1.0 g, at room temperature of 23 ±1°C and shaking was applied at 120 rpm for an equilibrium time of 15 h. The experimental conditions were obtained from the preliminary tests. The initial pH values were adjusted from 2 to 12 with 0.1M HCl or 0.1M NaOH using a pH meter (Quimis - model Q-400M_2).

Adsorption Kinetics

The solutions of each isolated compound were prepared with a different initial concentration of the BTX compounds (15 to 150 mg/L), containing the adsorbate of interest, placed in 250 mL Erlenmeyer flasks, closed with a Teflon stopper to avoid volatilization of the adsorbate, and then placed on a shaker (EQUILAM, model IB 9082A) tray inside a thermostatic bath, at a temperature of 23 ±1°C and shaken at 120 rpm (the two latter conditions being controlled). The maximum concentration of 150 mg/L was chosen respecting the solubility limit of o-xylene, in which exhibits the lowest solubility in water compared to benzene and toluene (water solubility of 175 mg/L). All experimental conditions were optimized in preliminary tests. The adsorbent mass used in the experiment was 1.0 g (for fixed conditions of concentration, pH, stirring speed and time, the mass of 1.0 g of adsorbent showed the largest adsorption capacity). The initial pH of the adsorption remained at around 6.4. The adsorption kinetics experiments were performed in duplicate using a 95% confidence limit.

Adsorption Equilibrium

The quantity of BTX adsorbed at equilibrium, q_e (mg/g), for each test, was calculated through the mass balance, considering that the contaminant which is not found in solution is adsorbed in the solid phase. All the results obtained experimentally for the adsorption equilibrium of the BTX compounds were fitted using the least-squares method with the software STATISTICA 7.0, applying the Langmuir and Freundlich adsorption isotherm models to the monocomponent compounds. The adsorption isotherm experiments were performed in duplicate using a 95% confidence limit.

RESULTS AND DISCUSSION

Characterization of Activated Carbon

It was verified by way of the physical and chemical analysis that the activated carbon used in the adsorption of the BTX compounds had a low moisture content (0.03% dry basis) and ash content (1.4% dry basis) and a high quantity of fixed carbon (94.99% dry basis). The determination of the surface functional groups by the Boehm titration method showed that the activated carbon used in this study had higher amounts of basic functional groups (8.19×10^{-4} mEq/(100 g)) compared to acid functional groups (mEq/100 2.86×10^{-4}), indicating that the carbon had a basic character. Also, lactones (4.35×10^{-5} mEq/(100 g)) and phenolic compounds (2.43×10^{-4} mEq/(100 g)) were present. The results for the textural characterization of the adsorbent indicated a surface area of 724 m^2/g. In relation to the extent of microporosity, the values obtained were: pore volume = 0.39 cm^3/g; average pore diameter = 21.35Å; micropore volume = 0.31 cm^3/g; micropore area = 614 m^2/g and the pore size was distributed between the minimum value of 18 Å and maximum value of 400 Å.

Figure 1 shows the results for the scanning electron microscopy (SEM) analysis of the adsorbent used in this study, where the magnifications of the micrographs are 30 and 125 times. It can be seen in Figure 1 that a large number of pores are present, as observed in the structural characterization of the adsorbent. Through the elemental analysis, it was confirmed that a high percentage of elemental carbon is present, and the second most abundant element was oxygen (around 9% by weight). Small amounts of Mg, Al, Si, K and Fe were also observed. These results indicate that the thermally-activated coconut shell carbon had a large surface area, large pore volume, and predominantly negative surface charge, which characterizes the coconut shell carbon as a good adsorbent for the removal by adsorption of BTX compounds, the molecules of which are weakly positively charged.

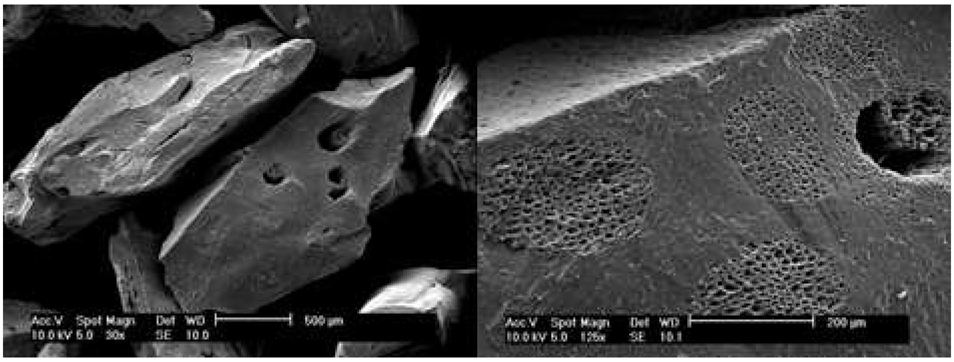


Figure 1. Micrographs of activated carbon originating from coconut shell.

Effect of pH

An increase in the pH did not influence the BTX adsorption by the adsorbent. This indicates that the adsorbent has high stability over the pH range of the solution (Su et al., 2010). Within the wide pH range studied there was no influence of pH on the adsorption capacity for BTX compounds, the average concentrations remaining in the solid phase being 122 mg/g, 149 mg/g and 164 mg/g for benzene, toluene and o-xylene, respectively.

These values are similar to those reported by Luz et al. (2013) for the maximum adsorption capacity for BTX compounds (124.77, 150.42 and 165.07 mg/g for benzene, toluene and o-xylene, respectively) using the same adsorbent. According to Villacañas et al. (2006), most aromatic contaminants are found in solution in the molecular state within a wide pH range. In this case, dispersive interactions are predominant and mainly caused by the attraction between the π orbitals of the basal carbon and the electronic density of the aromatic ring of the adsorbate (π–π interactions), according to Wibowo et al. (2007) and Yu et al. (2011).

However, when the solution pH is extremely high or extremely low, ions may be present, and electrostatic interactions between the functional groups and the carbon surface may be significant, which was not the case in this study. Similar results have been reported by Wibowo et al. (2007) and Yu et al. (2011). Since there was no variation in the adsorption of BTX compounds onto the activated carbon under the different pH conditions studied, we used the natural pH of the solution (approximately 6.4) to study the adsorption kinetics using different concentrations of adsorbate.

Equilibrium Study

1. Adsorption isotherms of BTX compounds

The parameters obtained for the adsorption of the BTX compounds are shown in Luz et al. (2013). The greatest adsorption capacity was observed for o-xylene, which had a larger structure, greater molar mass and lower water solubility. The values obtained for R^2 indicate that the two monocomponent adsorption isotherm models showed good fits with the experimental data, and the best average R^2 value for the compounds was obtained with the Langmuir isotherm.

2. Adsorption kinetics

The adsorption kinetics results describe the rate of solute removal, this being dependent upon the physical and chemical characteristics of the adsorbate, adsorbent and experimental system. Figure 2 shows the adsorption kinetics for the BTX compounds, that is, the concentration of contaminant present on the solid phase versus time [q_e (mg/g) versus t (min)].

On comparing the BTX compounds for a concentration of 15 mg/L, it can be noted that the efficiency of the adsorbent was highest for the removal of o-xylene. At 15 mg/L, the concentration of contaminant remaining at equilibrium was 3.02 mg/g for benzene, 3.36 mg/g for toluene, and 3.93 mg/g for o-xylene.

According to Shahalam et al. (1997), the adsorption of monocomponent BTX compounds occurs in the following order: xylene > toluene > benzene. The adsorption favoring this order of compounds may be explained by the reduction in solubility (B, 1790 mg/L > T, 530 mg/L > X, 175 mg/L) and the increase in the molecular mass (B, 78 g < T, 92 g < X, 106 g) and the boiling point (B, 80.1 °C < T, 110.7 °C < X, 144 °C).

On evaluating figure 2, it can be observed that there is a stage where there is a rapid increase in the solid phase concentration, where the kinetics is governed by the diffusion at the boundary layer and, for the rest of the curve, where the velocity is lower, there is a strong influence from the internal diffusion. Al-Duri and McKay (1992) related the internal diffusion to the ratio between the molecular diameter of the adsorbate and the adsorbent pore diameter, and proposed that the intraparticle diffusivity and adsorbent porosity are interdependent. They also observed a drop in the exponential effective diffusivity as the initial concentration of the contaminant increased in the fluid phase. The equilibrium times for the kinetics tests for 150 mg/L of the compounds benzene, toluene, and o-xylene were approximately 12 h, 8.5 h, and 13 h, respectively.

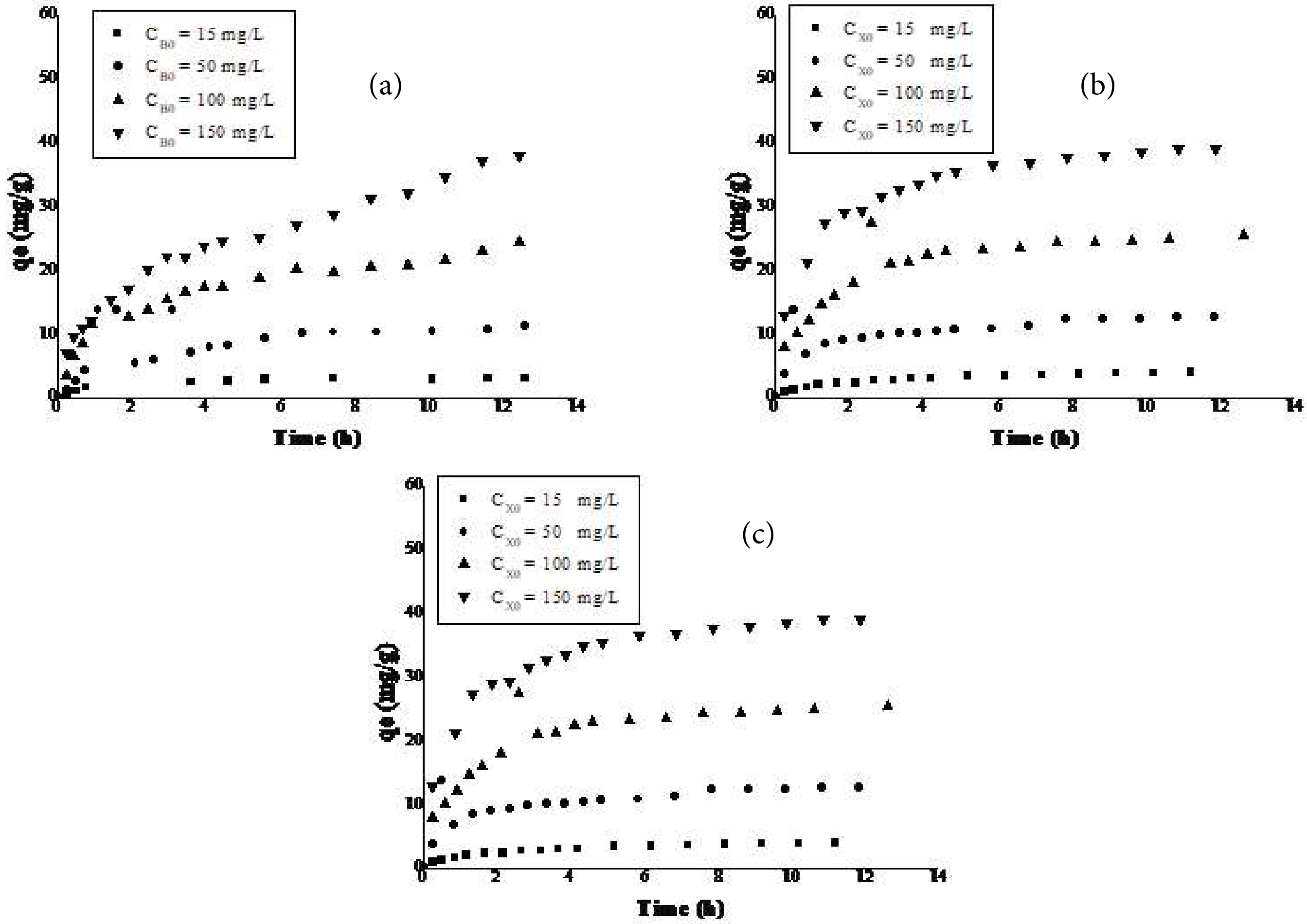


Figure 2. Monocomponent adsorption kinetics for BTX compounds: (a) Benzene, (b) Toluene and (c) o-Xylene: mass of adsorbent 1.0 g, volume 250 mL, temperature 23°C ±1°C.

3. Kinetic treatment

Pseudo-first-order model

The adsorption kinetics data were described by the Lagergren pseudo-first-order model (Ho e Mckay, 1998; Khaled et al., 2009; Nourmoradi et al., 2012), which is the earliest known equation describing the adsorption rate based on the adsorption capacity. According to some authors, the pseudo-first-order model can be related to the occurrence of physical adsorption, which may control the reaction rate (Cooney, 1999; Ho and McKay, 1999).

The Lagergren equation is commonly expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (1)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg.g^{-1}), and k_1 is the rate constant of pseudo-first-order adsorption (1/min). Integrating Eq. (1) for the boundary conditions t=0 to t = t and q_t =0 to q_t = q_t gives:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303}t \qquad (2)$$

Equation (2) can be rearranged to obtain the following linear form:

$$\log(q_e - q_t) = \log q_1 - \frac{k_1}{2.303}t \qquad (3)$$

Plot the values of log ($q_e - q_t$) versus t to give a linear relationship from which k_1 and q_e can be determined from the slope and intercept, respectively (Figure 3). If the intercept does not equal q_e then the reaction is not likely to be a first-order reaction even if this plot has a high correlation coefficient with the experimental data (Khaled et al., 2009). The variation in the rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between the initial solute concentration and the rate of adsorption will not be linear when pore diffusion limits the adsorption process.

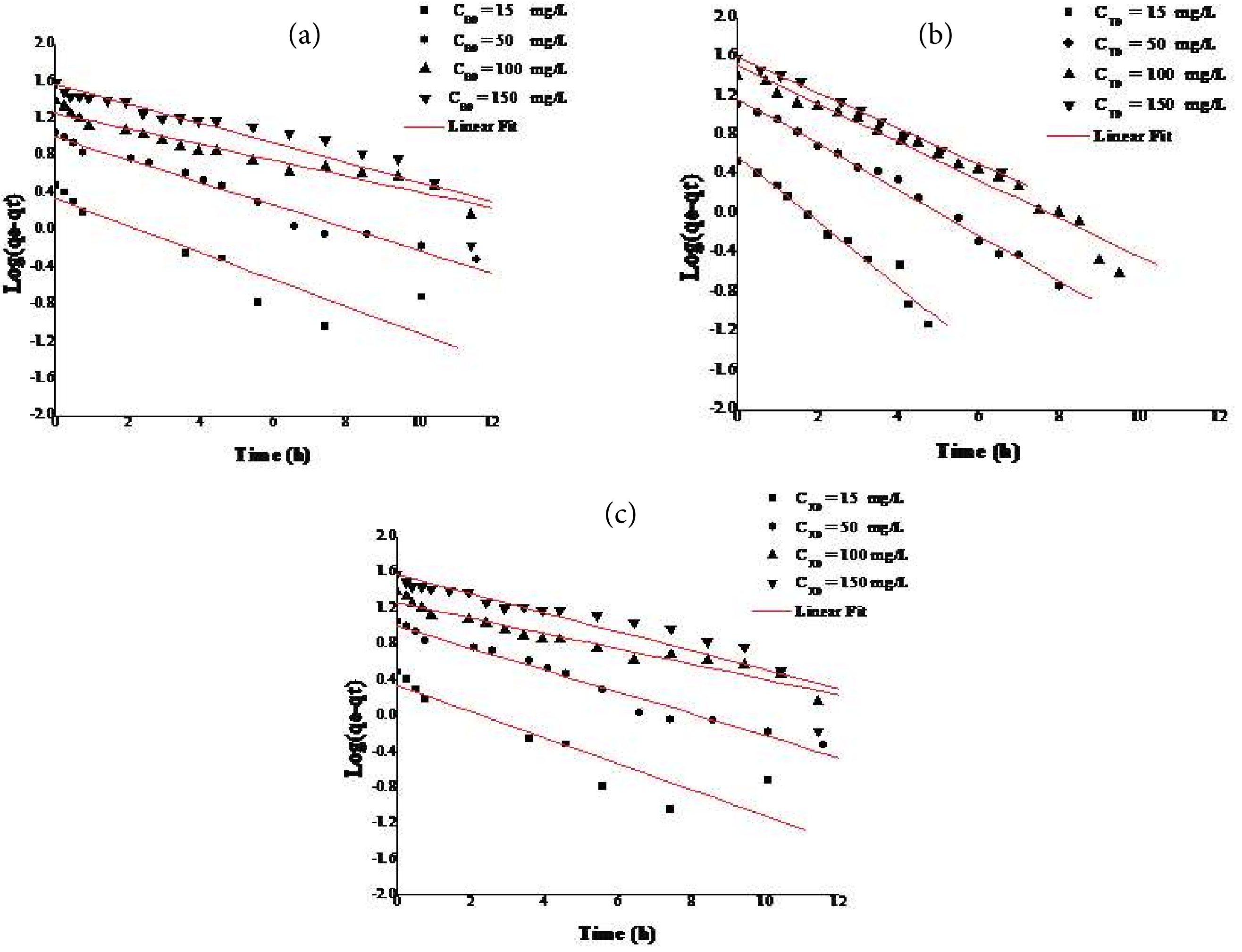


Figure 3. Pseudo-first-order kinetics for: (a) benzene, (b) toluene and (c) o-xylene: mass of adsorbent 1.0 g, volume 250 mL, temperature 23 ±1°C.

Figure 3 (a) - (c) shows the fitting of the pseudo-first-order adsorption kinetics data obtained for the BTX compounds. For the first 4 h, the data provide a good fit with the Lagergren model and thereafter the adsorption data deviate from the theoretical values. Thus, the model represents well the initial stages when rapid adsorption occurs, but it cannot be applied to the entire adsorption process. Furthermore, the calculated q_e values are too low compared with the experimental q_e values and the correlation coefficients (R^2) are relatively low for the most of the adsorption data (Table 1), which indicates that the adsorption of the BTX onto activated carbon does not occur through a first-order reaction. Aiming to better to characterize the kinetic process associated with this adsorbent a study applying the pseudo-second-order kinetic model was subsequently performed.

Pseudo-second-order model

The adsorption kinetics can be described by the pseudo-second-order model (Ho e Mckay, 1999; Khaled et al., 2009), which is generally given as follows:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (4)$$

where k_2 (g/mg min) is the second-order rate constant of adsorption. Integrating Eq. (4) for the boundary conditions $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$, this equation is simplified and can be rearranged and linearized to obtain:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \qquad (5)$$

The second-order rate constants were used to calculate the initial sorption rate, given by the following Eq. (6):

$$h = k_2 {q_e}^2 \qquad (6)$$

As mentioned above the curve fitting plots of log ($q_e - q_t$) versus t did not provide agreeable results for the entire sorption period, while the plots of t/q_t versus t gave a straight line for all the initial BTX concentrations studied, as shown in figure 4, confirming the applicability of the pseudo-second-order equation.

The higher linear correlation coefficient (R^2) of the pseudo-second-order model shows that this kinetic model fitted the data better than the other kinetic models described earlier (between 0.9641 and 0.9955). Moreover, the q_e calculated (mg/g) values using this kinetic model are reasonably similar to the q_e experimental (mg/g) values obtained from the experimental data. The pseudo-second-order kinetic parameters are presented in table 1.

As can be seen, the pseudo-second-order rate constant values, k_2 (g/mg h), are observed in the order of B > T > X, while the initial adsorption rate constant values of the pseudo-second-order kinetics, h (g/mg h), are shown to be in the order of B < T < X. The finding that the h value for xylene is higher than that of toluene following by benzene may be due to more external adsorption sites of the activated carbon being available at the beginning of the adsorption. Similar results were obtained by Nourmoradi et al. (2012).

Seifi et al. (2010) studied the kinetics of BTEX adsorption onto natural zeolite nanoparticles that were modified with surfactant and also found that the pseudo-second-order model best described the experimental data. In addition, Vidal et al. (2012) studied the kinetics of BTEX adsorption onto HDTMA-modified Y zeolite and found that the pseudo-second-order model best described the experimental data.

Therefore, compounds with higher hydrophilicity have a lower tendency to adsorb to the adsorbent, especially at the start of the process. But over the adsorption time, the k_2 value for benzene is higher than for toluene and then xylene. This may be attributed to the molecular mass of each BTX compound, that is, benzene, with a lower molecular mass, can more easily penetrate the adsorbent and reach the internal adsorption sites compared with toluene and then xylene.

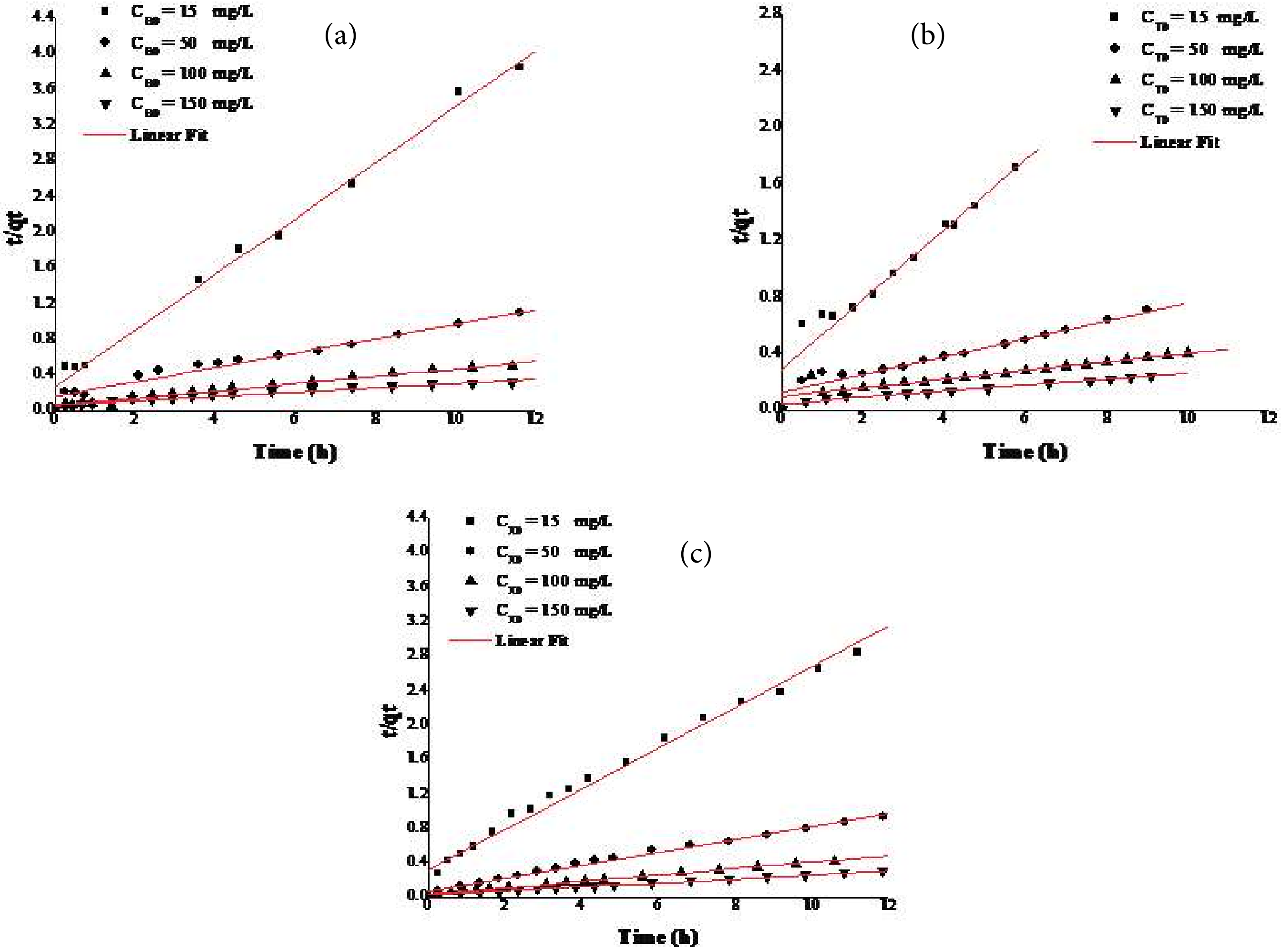


Figure 4. Pseudo-second-order kinetics for: (a) benzene, (b) toluene and (c) o-xylene. Mass of adsorbent 1.0 g, volume 250 mL, temperature 23 ±1°C.

Also, according to some authors, the pseudo-second-order model may be related to the occurrence of chemical adsorption, which could control the reaction rate (Ho and McKay, 1998). For the adsorbent under study, the elemental analysis were found small amounts of magnesium, aluminum, silicon, potassium and iron. These small quantities can be promoting a small chemical adsorption between the adsorbate and the adsorbent surface.

In general, it is concluded that the pseudo-second order model is appropriate to describe the adsorption process, however, through a detailed study from the kinetic experiments, it is possible to identify the stage that controls the adsorption process of the adsorbent. This study is done from the model intraparticle diffusion kinetic the kinetic data obtained experimentally.

Table 1. Comparison of the first and second-order adsorption rate constants for different initial concentrations of BTX compounds.

	q_e experimental (mg/g)	Parameters of the pseudo-first-order model			Parameters of the pseudo-second-order model			
		k_1 (1/h)	q_e (mg/g)	R^2	k_2 (g/mg h)	q_e (mg/g)	h_2 (mg/g h)	R^2
C_B (mg/L)								
15	4.027	0.3339	2.1414	0.8487	0.3667	3.1888	3.7288	0.9935
50	11.0659	0.2814	9.8855	0.9755	0.040	12.4378	6.1879	0.9715
100	24.3598	0.1962	17.9763	0.9428	0.03233	23.8663	18.4152	0.9853
150	37.7914	0.1927	32.2255	0.9641	0.02283	23.8663	13.0039	0.9641
C_T (mg/L)								
15	3.3646	0.7644	4.5914	0.9684	0.2178	3.7711	1.2627	0.9795
50	12.7443	0.5359	16.6945	0.9919	0.02499	14.6251	6.9649	0.9844
100	24.6417	0.4475	32.3624	0.9642	0.010	31.4267	10.9289	0.9955
150	37.8410	0.4194	52.2820	0.9952	0.00667	38.7525	17.5410	0.9909
C_X (mg/L)								
15	3.3646	0.7644	4.5914	0.9684	0.2178	3.7711	1.2627	0.9795
50	12.7443	0.5359	16.6945	0.9919	0.02499	14.6251	6.9649	0.9844
100	24.6417	0.4475	32.3624	0.9642	0.010	31.4267	10.9289	0.9955
150	37.8410	0.4194	52.2820	0.9952	0.00667	38.7525	17.5410	0.9909

The intraparticle difusion model

The intra-particular diffusion is commonly expressed by Eq. 7 (Ho e Mckay, 1998; Keith et al., 2004; Khaled et al., 2009):

$$q_t = k_{in} t^{1/2} \tag{7}$$

The intraparticle diffusion rate (kin), also known as the Weber Morris constant [mg/g ($h^{1/2}$)], is obtained through the linearization of the curve obtained from Eq. 7. The resulting graph can show multilinearity, indicating that two or more stages may limit the adsorption process, namely:

1 – A linear stage which begins with fast diffusion on the outer surface of the particle;

2 – A linear stage which begins with gradual adsorption, when the intraparticle diffusion is the step limiting; and

3 – An equilibrium stage in which intraparticle diffusion decreases due to a low concentration of solute in the solution, as well as a reduced availability of sites for adsorption (Seifi et al., 2010).

In all cases the quality of the fit obtained is given by the correlation coefficient R2. Figure 5 (a) - (c) shows the curve for q_t versus t^(1/2) for the intraparticle diffusion model, including the three stages mentioned above, for BTX compounds and table 2 presents the adsorption kinetics parameters of the intraparticle diffusion model obtained for BTX.

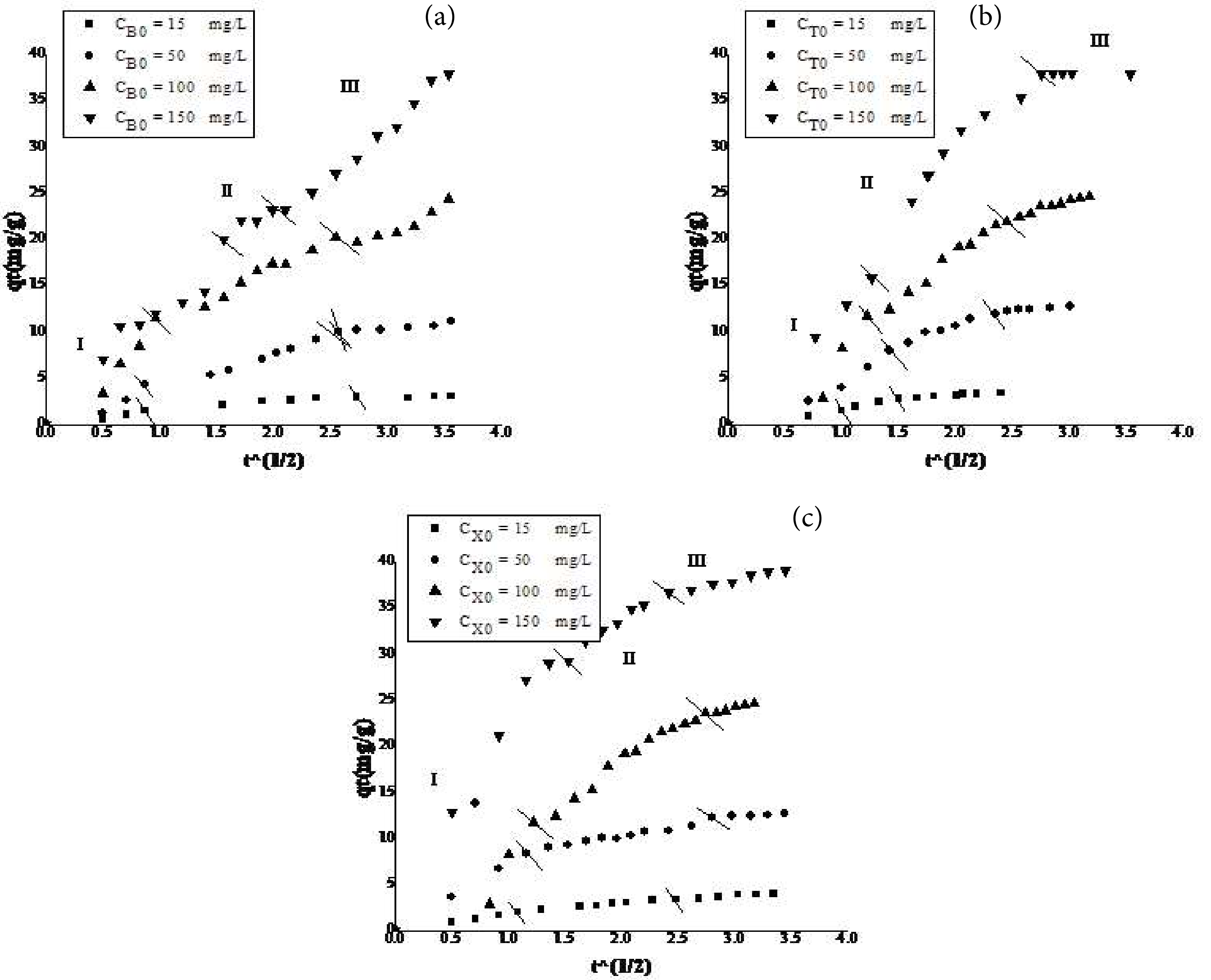
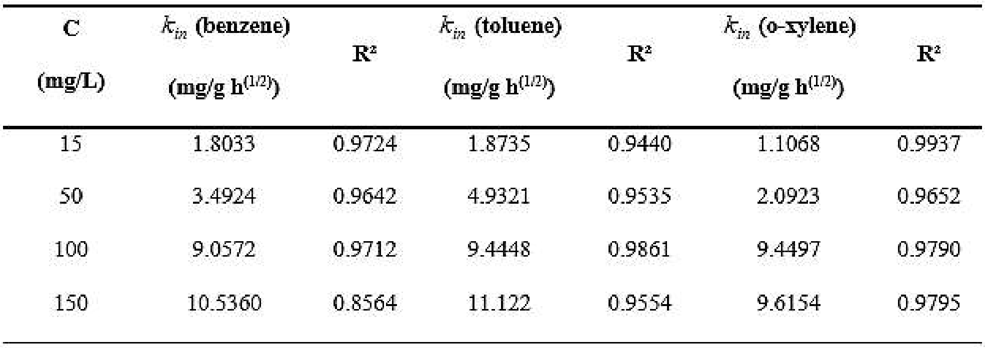


Figure 5. Fitting of adsorption kinetics parameters of the intraparticle diffusion model obtained for benzene, toluene and o-xylene: mass of adsorbent 1.0 g, volume 250 mL, temperature 23°C ±1°C.

It can be observed in table 2 that the intraparticle adsorption rate (k_{in}) increases with an increase in the concentration, this increase being greater for toluene, followed by benzene and lastly o-xylene. The observed order for these rates may be attributed to the mass and molecular configuration of the BTX compounds. The values for the intraparticle diffusion rate constant, k_{in}, were in the range of 1.1068 – 11.1220 mg/g $\text{min}^{1/2}$. The high values of the linear regression coefficients obtained for the second stage indicate that here the process is strongly controlled by intraparticle diffusion for all compounds studied at different concentrations.

Table 2. Kinetic parameters of the intraparticle diffusion model obtained for the BTX compounds.



C (mg/L)	k_{in} (benzene) (mg/g $h^{(1/2)}$)	R^2	k_{in} (toluene) (mg/g $h^{(1/2)}$)	R^2	k_{in} (o-xylene) (mg/g $h^{(1/2)}$)	R^2
15	1.8033	0.9724	1.8735	0.9440	1.1068	0.9937
50	3.4924	0.9642	4.9321	0.9535	2.0923	0.9652
100	9.0572	0.9712	9.4448	0.9861	9.4497	0.9790
150	10.5360	0.8564	11.122	0.9554	9.6154	0.9795

CONCLUSIONS

The adsorption kinetics for BTX compounds in a batch reactor was investigated for four different concentrations in aqueous solution at 23 ±1°C using thermally-activated coconut shell carbon as the adsorbent. The results showed that the thermal activation promoted an increase in the negative charge of the adsorbent which favored the adsorption of BTX molecules since BTX compounds have positive charges. The solution pH did not affect the adsorption of the molecules since the BTX are in the molecular state. In order to determine the limiting step of the adsorption process, the kinetics data were fitted to three different models: the pseudo-first order, pseudo-second order and intraparticle diffusion models. The pseudo-second order model was found to be the most efficient to describe the adsorption rate. For this model the correlation coefficient (R^2) varied between 0.995 and 0.9641 and the q_e calculated values were similar to the q_e experimental values. The values for the pseudo-second order rate constant, k_2, decreased in the order of B > T > X, while the initial adsorption rate constant values for the pseudo-second order kinetics, h, increased in the order of B < T < X. These results may be due to more external adsorption sites of the activated carbon being available at the beginning of the adsorption. Through a detailed study of the kinetics experiments it was possible to identify the stage that controls the BTX adsorption process by fitting the intraparticle diffusion model. The high values for the linear regression coefficients obtained for the second step indicated that the process is strongly controlled by intraparticle diffusion in the second stage for all compounds studied at different concentrations. Thus, understanding the adsorption mechanisms in several experimental conditions that occur between the adsorbent and the adsorbate on a bench scale is fundamental for the development of industrial projects. Besides that, the use of materials of vegetable origin have several advantages, such as low cost, abundance, renewability and are not toxic.

ACKNOWLEDGEMENTS

The authors are grateful to ANP/MECPETRO for financial support and to UFSC/LABSIN-LABMASSA for the infrastructure provided for this study.

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