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Benzene, toluene and *o*-xylene (BTX) removal from aqueous solutions through adsorptive processes

**Fabíola V. Hackbarth · Vítor J. P. Vilar ·
Geerlesson B. De Souza · Selene M. A. Guelli U. de Souza ·
Antônio Augusto U. de Souza**

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Abstract In this study, the monocomponent adsorption of benzene, toluene and *o*-xylene (BTX) compounds, as model contaminants present in the petrochemical wastewaters, was investigated using three types of adsorbents: activated carbon (Carbon CD 500), a polymeric resin (MN-202) and a modified clay (Claytone-40). Langmuir and Freundlich models were able to fit well the equilibrium experimental data. The BTX adsorption capacity increased in the following order: Claytone-40 < CD 500 < MN-202. The maximum uptake capacity of MN-202, given by the Langmuir fitting parameter, for benzene, toluene and *o*-xylene was 0.8 ± 0.1, 0.70 ± 0.08 and 0.63 ± 0.06 mmol/g at 26 °C. Desorption kinetics for polymeric resin with 50 % methanol solution were fast being able to reuse the resin in consecutive adsorption/desorption cycles without loss of sorption capacity. The adsorptive behaviour at batch system was modelled using a mass transfer kinetic model, considering that the sorption rate is controlled by a linear driving force model, which successfully predicts benzene, toluene and *o*-xylene concentration profiles, with homogeneous diffusivity coefficients, D_h, between 3.8×10^{-10} and 3.6×10^{-9} cm^2/s. In general, benzene diffuses faster than toluene and *o*-xylene, which is in agreement with molecular diffusivity in water.

Keywords Benzene · Toluene · *o*-Xylene · Adsorption · Modeling

List of symbols

a_p	Specific area for thin plates particles (1/cm)
C_b	BTX concentration in the liquid phase (mg or mmol adsorbate/L)
C_{b_0}	Initial BTX concentration in the liquid phase (mg or mmol adsorbate/L)
C_{BTX}	Equilibrium concentration of BTX in the fluid phase (mmol adsorbate/L)
D_h	Homogeneous diffusion coefficient (cm^2/s)
F_{cal}	Calculated value of F
F_α	Tabulated critical values for F distribution
$k_{1,ads}$	Adsorption constant of the pseudo-first-order model (h^{-1})
$k_{2,ads}$	Adsorption constant of the pseudo-second-order model (g adsorbent/mmol adsorbate/h)
k_p	Mass transfer coefficient for intraparticle diffusion (cm/s)
K_L	Equilibrium Langmuir constant (L/mmol adsorbate)
K_F	Equilibrium Freundlich constant (mmol$^{1-1/n}$L$^{1/n}$/g)
n	Empirical dimensionless parameter of Freundlich equation
$\langle q \rangle$	Average BTX concentration in the solid phase (mg or mmol adsorbate/g adsorbent)
q_{eq}	Solid phase concentration in equilibrium (mg or mmol adsorbate/g adsorbent)
q_i	Uptake capacity for each BTX (mg or mmol adsorbate/g adsorbent)

F. V. Hackbarth · G. B. De Souza ·
S. M. A. G. U. de Souza (✉) · A. A. U. de Souza
Laboratório de Transferência de Massa, Departamento de Engenharia Química e Engenharia de Alimentos,
Universidade Federal de Santa Catarina,
PO Box 476, Florianópolis 88040-900, SC, Brazil
e-mail: selene@enq.ufsc.br

V. J. P. Vilar (✉)
LSRE - Laboratory of Separation and Reaction Engineering – Associate Laboratory LSRE/LCM,
Faculdade de Engenharia, Universidade do Porto,
Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
e-mail: vilar@fe.up.pt

q_L	Maximum amount of BTX per g of adsorbent (mg or mmol adsorbate/L)
q_{BTX}	Equilibrium concentration of BTX in the adsorbent (mg or mmol adsorbate/g adsorbent)
q_t	Concentration of BTX in the sorbent at time t (mg or mmol adsorbate/g adsorbent)
$r_{ads}(i)$	Initial adsorption rate (mmol/g/h)
r	Dimensionless radial coordinate inside the particle
R	Radial position in the particle (cm)
R_0	Radius of the adsorbent particle (cm)
R^2	Regression coefficient
$S_R^2(A)$	Variance of model A
$S_R^2(B)$	Variance of model B
t	Time (h)
T	Temperature (°C)
V	BTX solution volume (L)
x	Dimensionless BTX concentration in the solid phase
$\langle x \rangle$	Dimensionless average BTX concentration in the solid phase
x_b	Dimensionless BTX concentration in the liquid phase
x^*	Dimensionless BTX concentration in the solid phase at the particle surface
W	Mass of adsorbent (g)
τ_d	Time constant for intraparticle diffusion (min)
α	Level of significance
σ_i	Relative standard deviation
ξ	Batch capacity factor

1 Introduction

Petrochemical wastewater treatment constitutes a big challenge for research community due to its complex mixture of hydrocarbons compounds, sulfur oxides, metals, and numerous toxic organic compounds (Fahim et al. 2010; Speight 2011). Botalova et al. (2009) presented a characterization of wastewaters from two different petrochemical companies and identified a large number of phosphorous, nitrogen, sulphur, oxygen-containing compounds as well as aliphatic and mono- or polycyclic aromatic hydrocarbons, including benzene, toluene and xylenes, known as BTX. Several of these compounds were also detected into the river, up to 15 km distance from the petrogenic emission, indicating the inefficiency of conventional refinery wastewater treatment plants for the complete elimination of these toxic compounds at trace levels. These compounds are extremely toxic, presenting chronic toxicity even at low concentrations (Adami et al. 2006; Giuliano et al. 2009; Moro et al. 2012; Ruchirawat et al. 2010; Mello et al. 2010). BTX compounds have been classified by USEPA as priority pollutants, which can represent a threat to the environment and to human health due to their toxic properties (Jo et al. 2008; Mello et al. 2010; Shim et al. 2002).

BTX removal from aqueous solutions has been reported using different methods, such as adsorption (Moura et al. 2011; Vidal et al. 2012; Lin and Huang 1999), advanced oxidation processes (Tiburtius et al. 2005; Wu et al. 2011) and biological (Farhadian et al. 2008; Kelly et al. 1996; Maliyekkal et al. 2004) processes. Each of these processes has advantages and disadvantages; however, adsorption offers a more efficient way to purify the effluent to a point where it is suitable for discharge into the environment (Lin and Huang 1999; Aivalioti et al. 2010; Ip et al. 2009).

Activated carbons are the main sorbents used nowadays at different industrial facilities regarding the elimination of different organic pollutants. Considering the costs associated to activated carbons production, as also regeneration, research has been oriented to the development of alternative sorbents, such as zeolites (Vidal et al. 2012; Alejandro et al. 2012), organosilicates (Moura et al. 2011), modified clays (Jaynes and Vance 1999; Aivalioti et al. 2010; Vianna et al. 2005) and polymeric resins (Da Silva et al. 2012; Lin and Huang 1999).

A high degree of selectivity compared with activated carbon was obtained with polymeric resins (Xu et al. 2003; Simpson et al. 1993). These ones are available with different degrees of hydrophobicity, pore size and surface area (Jr and Vliet 1981). After years of development, the porous resins have become efficient adsorbents not only for the treatment of industrial effluents, but also for the recovery of adsorbed organic chemical products for subsequent reuse (Xu et al. 2003). Lin and Huang (1999) evaluated the use of macroreticular resins, Ambersorb 563, 572 and 600, for BTEX removal from aqueous solutions. The authors observed that the adsorption characteristics of the three resins were similar for each BTEX compound. A theoretical model based on the empirical squared-driving force principle was adopted for describing the mass transfer between the aqueous phase and the solid phase (resin).

Several studies have been widely accomplished for the removal of BTX compounds from aqueous solution by modified clays (Seliem et al. 2011; Sharmasarkar et al. 2000; Nourmoradi et al. 2012; Redding et al. 2002; Koh and Dixon 2001; Aivalioti et al. 2010; Jaynes and Vance 1999; Vidal and Volzone 2009; de Paiva et al. 2008). The sorption of organic contaminants BTEX (benzene, toluene, ethylbenzene, *o*-, *m*-, *p*-xylene) in aqueous solutions was also studied using organo-modified minerals (Sharmasarkar et al. 2000). As compared to benzene and toluene, the large-size alkylbenzenes showed greater partitioning affinity due to their high hydrophobicity. The introduction of organic molecules, such as quaternary ammonium salts, modifies the nature of clays from hydrophilic to hydrophobic or organophilic, thus acquiring a high affinity to organic compounds (Yílmaz and Yapar 2004; de Paiva et al. 2008). The clays most commonly used to prepare organophilic clays are the bentonites (de Paiva et al. 2008). The synthesis of organoclays (bentonites, smectites or montmorillonites) is generally carried out using the ion exchange technique (Jaynes and Vance 1999).

Nourmoradi et al. (2012) showed that BTEX adsorption on modified montmorillonite was a physical, endothermic and spontaneous process. Because of high surface area, low cost, eco-friendly, non-toxicity and adsorption capacity of clays, this adsorbents can be considered as one of the effective options to remove BTEX from aqueous solution (Nourmoradi et al. 2012).

The main objective of this work is to evaluate the efficiency of alternative sorbents, polymeric resin (MN-202) and modified clay (Claytone-40), on the removal of benzene, toluene and *o*-xylene (BTX) compounds from aqueous solutions, as model contaminants present in petrochemical wastewaters. The efficiency of these alternative sorbents on BTX removal was also compared with a traditional activated carbon (Carbon CD500). Equilibrium isotherms and kinetics were obtained for each adsorbent using monocomponent BTX solutions. Desorption studies were also evaluated for the polymeric resin.

2 Experimental

2.1 Chemicals

Benzene (Fluka, 99.5 %), toluene (Vetec, 98 %), *o*-xylene (Sigma-Aldrich, 98 %) and methanol (Carlo Erba Gold) were HPLC analytical grade. BTX solutions were prepared by dissolving appropriate volumes of benzene, toluene and *o*-xylene in distilled water. Ultrapure water was obtained using a Milli-Q system (Millipore®, Bedford, MA, USA) with a resistivity of 18 MΩ cm.

2.2 Adsorbents

The purolite-macronet®MN-202 spherical resin particles were provided by the company Purolite (São Paulo, São Paulo, BR), and is characterized by a macroporous polystyrene crosslinked with divinylbenzene, without functional groups. It is a macroporous inert adsorbent particularly suitable for the sorption of high molecular weight organic molecules with lipophilic properties as are typically found in wastewaters from industrial processes, such as dyestuffs or pesticides. The MN-202 particles were washed with distilled water immediately before the laboratory tests, as recommended by the manufacturer.

The modified clay used in this study was provided by the company Southern Clay Products (SCP) (Gonzales, TX, USA), with commercial name Claytone-40. This is a modified montmorillonite using a quaternary ammonium salt (surfactant) with chemical name of dimethyl di(hydrogenated).

The activated carbon of vegetal origin was supplied by the company Peligrini Carbon (Simões Filho, Bahia, BR), with the specification activated carbon CD 500, which was manufactured from shell of the oil palm seed. The activated carbon was sieved to obtain a grain size of 20–30 mesh (0.595–0.841 mm), which was the range selected for this study. The sample was then washed with distilled water and dried in an oven at 105 °C for a period of 24 h and stored until use.

2.3 Adsorbents characterization techniques

Scanning electron microscopy (SEM) was carried out to obtain structural information, as well as the chemical composition of the adsorbents. This analysis was carried at the Central Laboratory for Electron Microscopy—LCME UFSC using the apparatus JEOL JSM-6390LV.

The surface functional groups were characterized using the titration method Boehm (Boehm 2002; Wibowo et al. 2007), where 1 g of adsorbent sample was placed in contact with 50 mL of the following solutions with a concentration of 0.1 mol/L: NaOH, Na_2CO_3, $NaHCO_3$ and HCl. The vials were sealed and stirred for 24 h. After this period, an aliquot of 10 mL was filtered, where the excess of base or acid was titrated with HCl (0.1 mol/L) or NaOH (0.1 mol/L), respectively. The number of acid groups present on the surface of the solid was determined considering that NaOH neutralizes carboxyl groups, lactones and phenols; Na_2CO_3 neutralized carboxyl groups and lactones, and $NaHCO_3$ neutralizes carboxyl groups only. The number of basic sites was calculated based on the amount of HCl that reacted with the adsorbent.

Textural characterization of the sorbent particles was carried out to obtain the surface area, pore volume, pore size distribution and particle irregularity. This analysis was carried out in an Autosorb 1C automatic adsorptometer (Quantachrome, USA), at the Analysis Center of the Chemical and Food Engineering Department, Federal University of Santa Catarina (UFSC).

2.4 Kinetic studies

The monocomponent adsorption kinetics were carried out in a batch system, using a 275 mL Erlenmeyer flask closed with a Teflon stopper to avoid volatilization of the adsorbate. The flasks were placed on an orbital shaker, which is inside a thermostatic bath, allowing controlled temperature conditions. The reactor was filled with 275 mL of benzene, toluene, *o*-xylene solutions with concentrations of 60 and

150 mg/L and a known amount of adsorbent (2 g of CD 500, 2 g of MN-202 and 6 g of Claytone-40). The suspension was stirred at 150 rpm under controlled temperature (26 ± 2 °C). The initial solution pH was around 7.2 for CD 500, 5.4 for MN-202 and 6.4 for Claytone-40. Samples (0.5 mL) were collected at predetermined time intervals and filtered by polypropylene membrane filters (pore size of 0.20 µm). The benzene, toluene and *o*-xylene concentrations were determined by HPLC.

Desorption experiments with benzene and toluene saturated resin MN-202 were carried out by adding 275 mL of a 50 % methanol solution to 2 g of resin. The Erlenmeyer flasks were placed on an orbital shaker (120 rpm), which is inside a thermostatic bath, allowing a controlled temperature of 26 ± 2 °C. After each desorption test, the adsorbent was washed with distilled water several times to remove the solvent in excess and subjected again to the adsorption process.

2.5 Equilibrium studies

BTX adsorption equilibrium studies for the three adsorbents were carried out in a batch system, using a 275 mL Erlenmeyer flask closed with a Teflon stopper to avoid volatilization of the adsorbate. The flasks were placed on an orbital shaker, which is inside a thermostatic bath, allowing controlled temperature conditions. The flasks were filled with 275 mL of benzene, toluene or *o*-xylene solution with concentrations of 20, 40, 60, 80, 100, 120 and 150 mg/L and a known amount of adsorbent (2 g of CD 500; 2 g of MN-202 and 6 g of Claytone-40). The suspension was stirred at 150 rpm under controlled temperature (26 ± 2 °C). After the system reached equilibrium (24 h for CD 500; 30 h for MN-202 and 3 h for Claytone-40), samples were collected, filtered (polypropylene membrane filters, pore size of 0.20 µm) and the remaining benzene, toluene and *o*-xylene concentrations were determined by HPLC. All the equilibrium tests were carried out in triplicate.

2.6 Analytical methods

BTX compounds concentrations were determined by high performance liquid phase chromatography-HPLC (Shimadzu, CLASS-VP) equipped with a SPD-10A VP UV/visible detector and LC-10AT VP pump. The reverse-phase column (Nucleosil C18, internal diameter of 4.6 mm, length 250 mm) was operated at room temperature (25 °C). The mobile phase was prepared daily in proportions of 80:20 (methanol/Milli-Q water), and delivered at a flow rate of 1.0 mL/min in isocratic mode during 12 min. Injection volume was 20 µL and the wavelength of the UV absorbance detector was set at 254 nm.

2.7 Parameter estimation

The mathematical models were fitted to the experimental data obtained from equilibrium and kinetic studies using a non-linear regression method (Biosoft Fig. P for Windows). The model parameters were obtained by minimizing the sum of the squared deviations between experimental and predicted values. The goodness of fit of the model was evaluated through the calculation of the relative standard deviations (σ_i) and the regression coefficients (R^2). The performances of the two equilibrium models were compared using an *F* test (Montgomery 2001). F_{cal} is defined as $F_{cal} = \frac{S_R^2(A)}{S_R^2(B)}$, where $S_R^2(A)$ and $S_R^2(B)$ are, respectively, the variances of models A and B. F_α and α are, respectively, the tabulated critical values and the level of significance. In general, the residual variance of the model expected to produce the best fit is placed in the denominator (model B). If $F_{cal} > F_\alpha$, the model corresponding to the denominator is statistically better than the other, according to the chosen confidence level ($1 - \alpha = 0.95$).

3 Results and discussion

3.1 Characterization of the adsorbents

The elementary analysis confirmed that the element carbon is the main constituent of the activated carbon (>99 %). The polymeric resin presents a lower carbon content (76 %), followed by nitrogen (15 %) and small amounts of bismuth (5 %), oxygen (2 %) and chlorine (2 %). The modified clay presents 37 % of carbon, showing its organophilic character, as also silicon (28 %), oxygen (14 %) and aluminium (9 %), which is the base of montmorillonite clay group (Liu et al. 2008; Tiwari et al. 2008).

The Boehm titrimetric results showed that activated carbon present a slight higher amount of basic functional groups (0.16 meq/g) when compared with acid groups (0.12 meq/g), showing its basic nature. The basicity of the activated carbon is extensively mentioned in the literature (Montes-Morán et al. 2012; Fuente et al. 2003; Menéndez et al. 1996). Different studies reported that the basicity nature of activated carbons favours the adsorption of organic compounds in aqueous solution (Franz et al. 2000; Kaneko et al. 1989; Villacañas et al. 2006; Wibowo et al. 2007). Water can adsorb by means of hydrogen bonding on acid oxygen-containing functional groups followed by clustering of additional water molecules at these sites. The resulting water clusters can prevent pollutant access to hydrophobic regions on the activated carbon surface, reducing the interaction energy between the organic pollutant and the adsorbent surface (Villacañas et al. 2006).

Claytone-40 presents almost the same amount of acid (0.10 meq/g) and basic groups (0.09 meq/g). According to the manufacturer, a MN-202 polymeric resin does not have functional groups.

Textural characteristics of the adsorbents are reported in Table 1, showing that although the MN-202 resin has a specific surface area similar to the activated carbon, it presents a much higher pore volume, indicating a high porosity. On the other hand, the modified clay has a small specific surface area and pore volume, which can be associated to the size of the space occupied by the salt molecules used in the organophilization process acting as a plug to the N_2 probe molecules (Jiang et al. 2002). The decrease of the surface area of bentonite with increasing degree of modification is consistent with the results of previous studies (Jiang et al. 2002; Jiang and Zeng 2003; Yílmaz and Yapar 2004; Akcay 2004). Yílmaz and Yapar (2004) found a specific surface area of 30 m^2/g for a natural bentonite and 13 and 10 m^2/g for bentonite modified with tetradecyl trimethylammonium bromide and hexadecyl trimethylammonium bromide, respectively.

Figure 1 shows the results of the SEM analysis for the adsorbents used. Analysing the images, it can be observed that the activated carbon CD 500 (Fig. 1a) has an irregular surface with a large porosity. On the other hand, the resin MN-202 spherical particles (Fig. 1b) showed a tendency not associative, forming not agglomerated particles. The image magnification 10,000× can visualize their porous surface, consistent with the data presented in Table 1. Images of modified clay Claytone-40 (Fig. 1c) indicate a smooth and homogeneous morphology with leaves crowded and with a low thickness.

3.2 Adsorption isotherms

The adsorption isotherms for the three pollutants, benzene, toluene and *o*-xylene, using the three types of adsorbents are presented in Fig. 2. The amount of BTX removed per gram of the solid adsorbent was calculated using the mass conservation balance to the batch system (Eq. 1):

$$q_i = \frac{V}{W}\left(C_{b_0,i} - C_{b,i}\right) \quad (1)$$

where q_i is the uptake capacity for each BTX (mmol BTX/g of the adsorbent), V (L) the volume of solution, W (g) the dry weight of the sorbent added, $C_{b_0,i}$ (mmol/L) and $C_{b,i}$ (mmol/L) the initial and final BTX concentrations in the solution, respectively.

The Langmuir (1918) and Freundlich (1907) equilibrium models were fitted to the equilibrium data, represented by the following equations, respectively:

$$q_{BTX} = \frac{q_L K_L C_{BTX}}{1 + K_L C_{BTX}} \quad (2)$$

and

$$q_{BTX} = K_F (C_{BTX})^{(1/n)} \quad (3)$$

where q_L (mmol/g) is the maximum uptake capacity of each BTX compound per unit weight of adsorbent in the Langmuir equation, C_{BTX} and q_{BTX} are the equilibrium concentrations of each BTX in liquid (mmol/L) and solid phase (mmol/g), respectively, K_L (L/mmol) reflects the affinity of the adsorbent for the BTX compounds, K_F ($mmol^{1-1/n} L^{1/n}/g$) is an indicator of the adsorption capacity and n is an empirical parameter of the Freundlich equation. Values of n higher than 1 indicates that the affinity between adsorbent and adsorbate is relatively strong (Koyuncu et al. 2011). Nourmoradi et al. (2012) and Sharmasarkar et al. (2000) reported n values for BTEX removal using modified montmorillonite-PEG-Mt and organo-clays Wyoming montmorillonite (SWy) modified with three organic cations (trimethylphenylammonium (TMPA), trimethylammonium adamantane (Adam), and hexadecyltrimethylammonium (HDTMA), respectively, in the range of 1.31–1.88.

The adequacy of the two models was compared using the statistical F test. For a 95 % confidence level, no statistical difference between the two models was observed. So, results will be compared using the Langmuir model parameters.

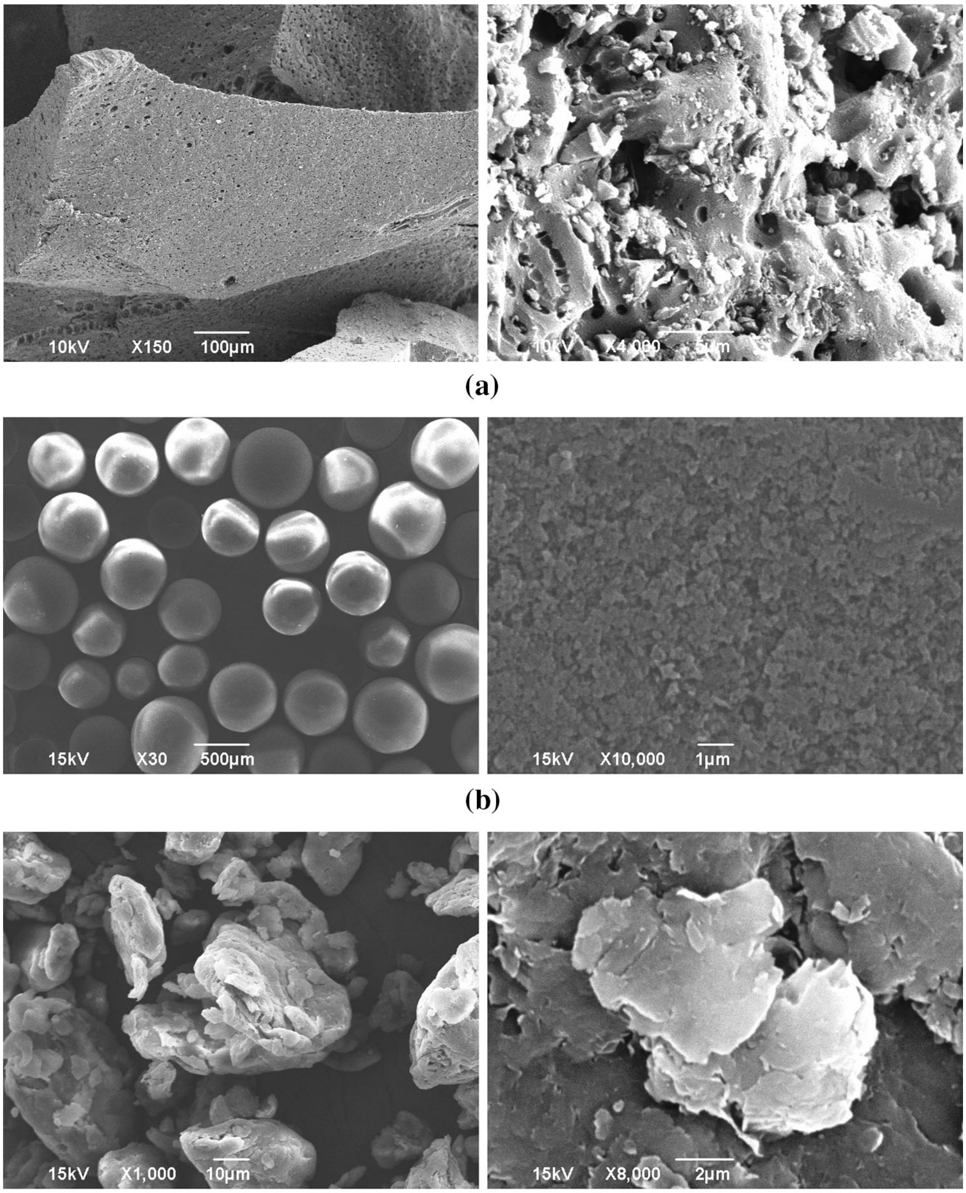
Figure 2 shows that the Langmuir model fits well the experimental equilibrium data for all the BTX compounds/adsorbent systems. The estimated Langmuir and Freundlich parameters are summarized in Table 2.

Comparing the different adsorbents, the MN-202 resin has a similar BTX adsorption capacity to the activated carbon CD 500, and more than four times higher than for the Claytone-40. An interesting finding is that the adsorption capacity of each adsorbent is similar for benzene, toluene and *o*-xylene. However, the BTX compounds have a different affinity to each adsorbent, increasing in the following order benzene < toluene < *o*-xylene.

Table 1 Textural characteristics of adsorbents used in adsorption of BTX compounds

Characteristics	CD 500	MN-202[a]	Claytone-40
Surface area (m^2/g)	657	700	14
Apparent density (ρ_{ap}) (g/cm^3)	0.45–0.55	1.0	1.7
Particle diameter (d_p) (μm)	595–841	450–620	75
Pore volume (cm^3/g)	0.36	1.00	0.02
Average pore diameter (Å)	17.5	15.0	14.9
Micropore volume (cm^3/g)	0.26	–	0.008
Micropore area (m^2/g)	451	–	10
Particle pore distribution (Å)	7–360	–	10–360

[a] Information obtained from the manufacturer



(a)

(b)

(c)

Fig. 1 SEM micrographs of the **a** activated carbon CD 500, **b** resin purolite-macronet®MN-202 and **c** modified clay Claytone-40

Adsorption capacities of the adsorbents presented in this work are comparable to most of the adsorbents used for BTX compounds removal from aqueous solutions (Table 3).

3.3 Adsorption kinetics

Figure 3 shows the kinetic profiles of BTX adsorption in the three selected materials. The BTX removal efficiency was higher than 83 % for all the adsorbents tested (for each adsorbent it was used a different solid/liquid ratio in order to have an equilibrium BTX concentration significantly lower than the initial one), with the exception for the system modified clay/benzene (69 %). Thus, all the adsorbents exhibited the ability to reduce the BTX concentration to low residual levels.

For the interpretation of the kinetic data a pseudo-first-order kinetic model (Eq. 4) (Lagergren 1898) and a pseudo-second-order kinetic model (Eq. 5) (Ho 1995) were used.

Pseudo-first-order model

$$q_t = q_{eq}\left[1 - \exp\left(-k_{1,ads}t\right)\right] \tag{4}$$

Pseudo-second-order model

$$q_t = \frac{q_{eq}^2 k_{2,ads} t}{1 + k_{2,ads} q_{eq} t} \tag{5}$$

where, q_t is the concentration of the BTX compound in the adsorbent at time t (mmol BTX/g adsorbent), q_{eq} is the equilibrium concentration of the BTX compound in solid phase (mmol/g), $k_{1,ads}$ is the adsorption constant of the

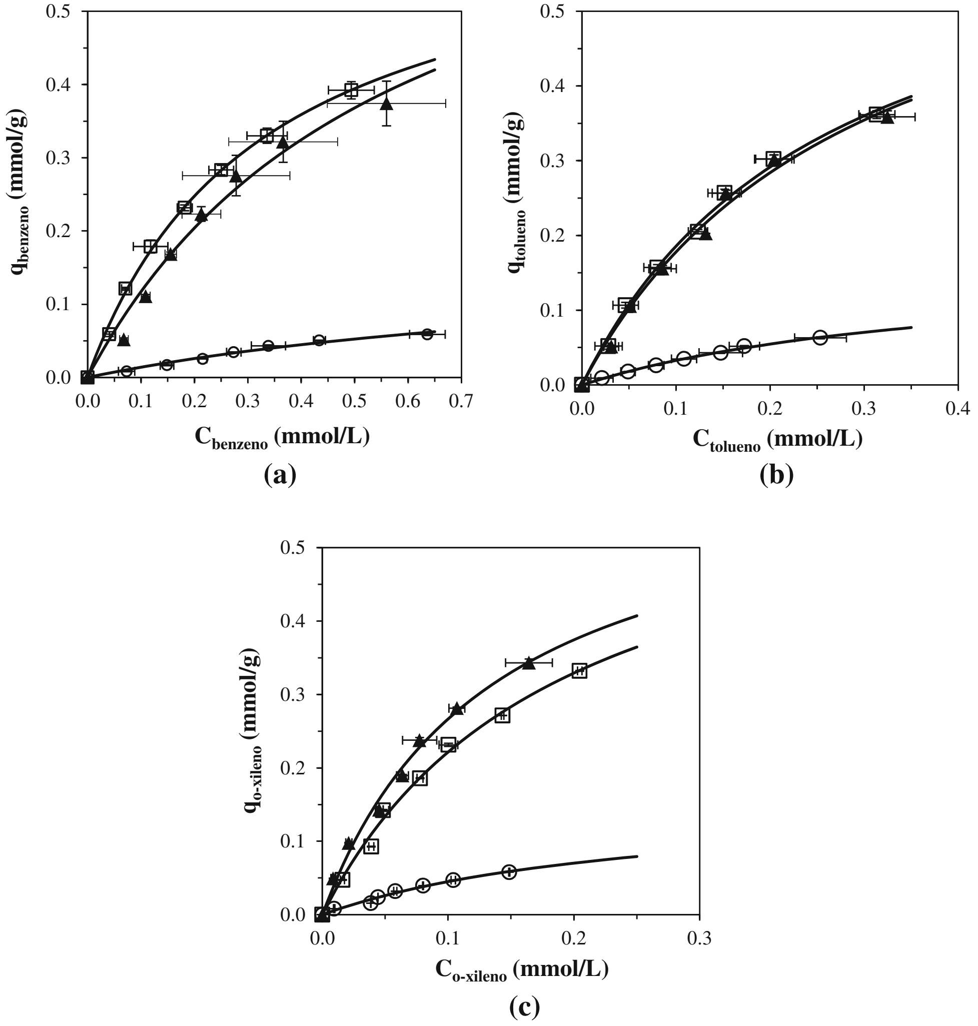


Fig. 2 **a** Benzene, **b** toluene and **c** *o*-xylene adsorption isotherms for different adsorbents (average q_{BTX} and C_{BTX} ± standard deviation). *Square* CD 500, *triangle* MN-202, *circle* Claytone-40, *horizontal bar* Langmuir Model

Table 2 Equilibrium parameter of adsorption isotherms obtained for the BTX compounds on different adsorbents

	Langmuir				Freundlich			
	q_L (mmol/g)	K_L (L/mmol)	R^2	S_R^2 (mmol/g)^2	n	K_F (mmol$^{1-1/n}$L$^{1/n}$/g)	R^2	S_R^2 (mmol/g)^2
Benzene								
CD 500	0.65 ± 0.03	3.1 ± 0.2	0.999	3.8×10^{-4}	1.6 ± 0.1	0.63 ± 0.03	0.988	2.6×10^{-4}
MN-202	0.8 ± 0.1	1.7 ± 0.5	0.985	3.5×10^{-4}	1.4 ± 0.2	0.60 ± 0.06	0.965	7.3×10^{-4}
Claytone-40	0.17 ± 0.04	0.9 ± 0.3	0.984	8.5×10^{-6}	1.3 ± 0.1	0.090 ± 0.007	0.973	1.4×10^{-5}
Toluene								
CD 500	0.68 ± 0.05	3.8 ± 0.5	0.995	8.5×10^{-5}	1.5 ± 0.1	0.81 ± 0.07	0.985	2.9×10^{-4}
MN-202	0.70 ± 0.08	3.4 ± 0.7	0.991	1.7×10^{-4}	1.5 ± 0.1	0.81 ± 0.09	0.977	4.2×10^{-4}
Claytone-40	0.17 ± 0.02	2.4 ± 0.3	0.997	1.4×10^{-6}	1.32 ± 0.06	0.18 ± 0.01	0.995	2.8×10^{-6}
o-Xylene								
CD 500	0.64 ± 0.06	5.3 ± 0.8	0.994	8.8×10^{-5}	1.5 ± 0.1	1.0 ± 0.1	0.986	2.1×10^{-4}
MN-202	0.63 ± 0.06	7 ± 1	0.993	1.3×10^{-4}	1.58 ± 0.09	1.1 ± 0.1	0.992	1.4×10^{-4}
Claytone-40	0.16 ± 0.04	4 ± 1	0.984	7.4×10^{-6}	1.3 ± 0.1	0.26 ± 0.04	0.981	8.8×10^{-6}

Table 3 Adsorption capacity of various adsorbents as reported in literature

Material	Adsorption capacity (mmol/g)			pH	T (°C)	References
	Benzene	Toluene	*o*-Xylene			
Claytone-40	0.17	0.17	0.16	6.4	26	This study
PEG-Montmorillonite	0.08	0.07	0.08	7	25	Nourmoradi et al. (2012)
TMA-Montmorillonite	–	0.2	–	–	–	Vidal and Volzone (2009)
Montmorillonite	0.4	0.3	–	–	–	Koh and Dixon (2001)
Smectite organoclay	0.007	0.007	–	9	23	Carvalho et al. (2012)
Treated nanozeolites	0.01	0.009	–	9	23	Seifi et al. (2011)
Thermally modified diatomite	0.004	0.003	0.006	9	23	Aivalioti et al. (2010)
Purolite-macronet®MN-202	0.8	0.70	0.63	5.4	26	This study
Polymeric sorbents-XAD4	1.9	1.9	–	–	25	Simpson et al. (1993)
Polymeric sorbents-XAD2	0.9	1.0	–			
Polymeric sorbents-AC-F400	4.1	3.7	–			
Polymeric sorbents-FCMPS-CMME	–	16	–	–	25	Simpson et al. (1996)
Polymeric sorbents-FCMPS-CMEE	–	17	–			
Polymeric sorbents-FCMPS-XDC	–	10	–			
Polymeric sorbents-PSDVB	–	11	–			
Amberlite XAD-4	2.6	–	–	–	25	Azanova and Hradil (1999)
Lewatit EP63	3.6	–	–			
Hypercrosslinked resin Sample 390	3.8	–	–			
ethylene dimethacrylate polymer	1.1	–	–			
Carbon CD-500	0.65	0.68	0.64	7.2	26	This study
AC-F-400	2.3	2.1	–	7	30	Wibowo et al. (2007)
Coal-tar-derived activated carbon	11	13	–	–	–	Asenjo et al. (2011)
Carbon 119	1.5	1.4	1.3	6.4	23	de Souza (2012)
AC-DP	0.1	0.05	–		25	Daifullah and Girgis (2003)
AC-OS	0.1	0.06	–			
Active carbon	2.2	–	–	3	20	Liang and Chen (2010)
AC-F-300	–	2.9	–	–	25	Chatzopoulos et al. (1993)
AC41	8	16.5	–	6.8	20	Cotoruelo et al. (2007)
AC	3.5	–	–	6-9	30	Li et al. (2009)
ACO1	3.4	–	–			
ACO2	3.2	–	–			
ACD	3.4	–	–			

pseudo-first-order model (1/h) and $k_{2,ads}$ is the adsorption constant of the pseudo-second-order model (g adsorbent/mmol BTX/h).

The initial adsorption rate ($r_{ads}(i)$) can be calculated from:

$$\left.\frac{dq}{dt}\right|_{t=0} = r_{ads}(i) \tag{6}$$

Thus,

$$r_{ads}(i) = k_{1,ads} q_{eq} \tag{7}$$

and

$$r_{ads}(i) = k_{2,ads} q_{eq}^2 \tag{8}$$

for the pseudo-first-order (Eq. 7) and pseudo-second-order (Eq. 8) models, respectively.

The pseudo-second-order model provides a better fit to the experimental results, considering a level of confidence of 95 %, according to the *F* test. According to Fig. 3 and Table 4, removal of BTX compounds is faster using the Claytone-40, followed by activated carbon CD 500 and resin MN-202, achieving the equilibrium in 20, 500 and 1250 min. Claytone-40 presents a low porosity and surface area, and consequently the BTX adsorption in mainly at the exterior surface area. According Koh and Dixon (2001), the small clay particles facilitate the adsorption of organic compounds. Carvalho et al. (2012) obtained also a high adsorption rate within the first 10 min, reaching the

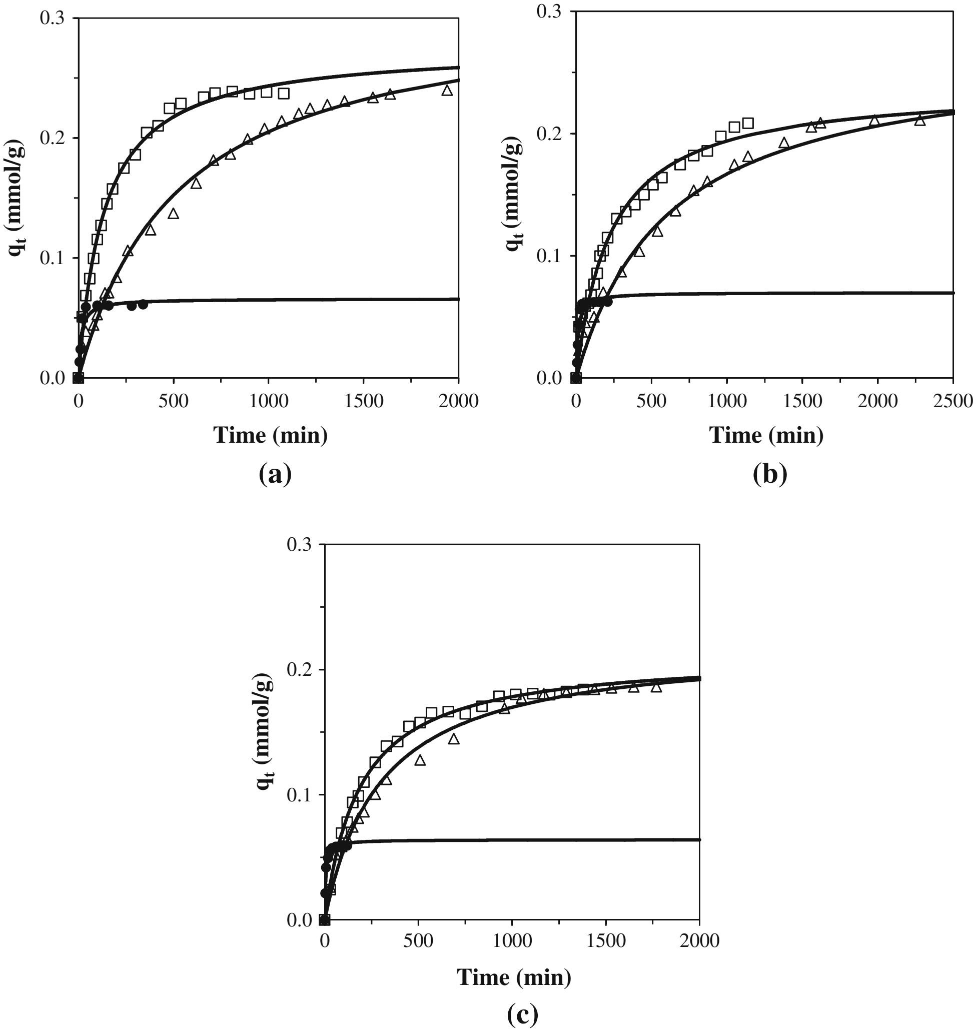


Fig. 3 Evolution of concentration **a** benzene, **b** toluene and **c** *o*-xylene adsorbed on different adsorbents with contact time: experimental data and predicted profiles. *Square* CD 500, *triangle* MN-202, *circle* Claytone-40, *horizontal bar* pseudo-second-order model. (C_i BTX = 150 mg/L)

Table 4 Kinetic parameters of the pseudo-second-order model for the adsorption of BTX compounds

Adsorbent	Adsorbate	k_2 (g/mmol/h)	q_{eq} (mmol/g)	$r_{ads(i)}$ (mmol/g/h)	R^2	S_R^2 (mmol/g)^2
CD 500	Benzene	$(2.7 \pm 0.2) \times 10^{-2}$	0.276 ± 0.004	$(2.0 \pm 0.2) \times 10^{-3}$	0.994	3.3×10^{-5}
	Toluene	$(1.8 \pm 0.2) \times 10^{-2}$	0.239 ± 0.007	$(1.0 \pm 0.1) \times 10^{-3}$	0.980	7.0×10^{-5}
	o-Xylene	$(2.5 \pm 0.1) \times 10^{-2}$	0.212 ± 0.002	$(1.00 \pm 0.04) \times 10^{-3}$	0.996	1.0×10^{-5}
MN-202	Benzene	$(6.0 \pm 0.5) \times 10^{-3}$	0.314 ± 0.008	$(6.0 \pm 0.6) \times 10^{-4}$	0.992	4.8×10^{-5}
	Toluene	$(6 \pm 1) \times 10^{-3}$	0.27 ± 0.01	$(4.0 \pm 0.7) \times 10^{-4}$	0.982	8.9×10^{-5}
	o-Xylene	$(1.5 \pm 0.1) \times 10^{-2}$	0.221 ± 0.004	$(7.0 \pm 0.5) \times 10^{-4}$	0.990	3.7×10^{-5}
Claytone-40	Benzene	1.1 ± 0.4	0.066 ± 0.004	$(5 \pm 2) \times 10^{-3}$	0.922	4.5×10^{-5}
	Toluene	1.1 ± 0.4	0.070 ± 0.005	$(5 \pm 2) \times 10^{-3}$	0.922	4.2×10^{-5}
	o-Xylene	2.8 ± 0.4	0.064 ± 0.002	$(1.0 \pm 0.2) \times 10^{-2}$	0.982	7.4×10^{-6}

equilibrium after a contact time of 60 min for the BTEX and phenol adsorption onto smectite organoclay.

Several mechanisms or combinations of mechanisms have been proposed for the adsorption of organic compounds on organophilic clays (Chen et al. 2002; Sheng et al. 1996). Aromatic molecules, due to their planar shape and delocalized π-bonds, interact strongly with organic cations, causing a reorientation of the alkyl chains. These solute molecules solvate the cationic ammonium centers and alkyl chains of $[(CH_3)_3NR]^+$, causing a transition from a parallel to more vertical position relative to the silicate sheets. Solute molecules are concomitantly adsorbed on the vacated mineral surfaces, which are hydrophobic in nature. Solute partitioning into the organic cations phase is also an important concurrent mechanism. The combination of solvation and partitioning produces substantially higher sorption of aromatic hydrocarbons than of aliphatic hydrocarbons (Chen et al. 2002; Sheng et al. 1996).

Removal of BTX compounds by the activated carbon and polymeric resin is faster at the initial stage and gradually decreases with time until saturation. This is attributed to the diffusion of the BTX molecules into the internal pores, as those adsorbents have a high surface area and porosity. Aromatic compounds adsorption onto activated carbons at liquid phase has been attributed mainly to two types of interactions: electrostatic and dispersive (Villacañas et al. 2006). The presence of basic functional groups on the activated carbon CD 500 favour the specific interactions between π orbital on the carbon basal plane and the aromatic rings of benzene, toluene and *o*-xylene, thus enhancing the adsorption (Wibowo et al. 2007).

Streat and Sweetland (1998) showed that the adsorption of organic compounds on porous resins can be attributed to several types of molecular interactions, including hydrophobic interaction, hydrogen bonding, ionic attraction and the formation of complexes. The binding energies of hydrophobic interaction and hydrogen bonds are relatively weak, indicating that organic compounds can be easily desorbed and recovered for reuse. The great advantage of the polymeric resins, beyond its chemical and physical stability and high surface area, is the easy regeneration, being possible to be used in consecutive adsorption/desorption cycles without loss of efficiency (Xu et al. 2003).

The resin MN-202 was developed especially for the removal of organic compounds and this adsorbent is easily regenerated using a variety of solvents such as methanol, ethanol, isopropyl alcohol, acids and caustic soda, and the choice depends on the desorbing agent organic compound adsorbed (Purolite 2013).

Desorption of benzene and toluene from MN-202 resin (Fig. 4) was evaluated using a 50 % methanol solution at batch system. The desorption efficiency was 73 and 63 % for benzene and toluene respectively. Desorption kinetics for benzene (300 min) were faster than for toluene (600 min) indicating that toluene binds strongly to the resin, which is in agreement with the Langmuir affinity constant values (K_L) presented in Table 2.

Although the resin adsorption capacity at the second adsorption cycle decreases 19 % for benzene and 22 % for toluene, considering the cumulative effect of the benzene and toluene compounds on the adsorbent, since the desorption process was not 100 % efficient, the adsorption capacity increased 9 and 14 % relatively to the first adsorption cycle. Due to its relative purity, the polymeric resins are highly durable. Streat and Sweetland (1998) have reported that there was no apparent degradation of adsorbents resins after two years and 1,300 cycles of operation for the recovery of phenol. According to Xu et al. (2003) less than 5 % annual replacement of the adsorbent were required for an operation of fluidized bed adsorption. Experiences in large scale in China confirmed that the life of polymeric resins can be more than five years with more than 2,000 cycles of regeneration (Xu et al. 2003).

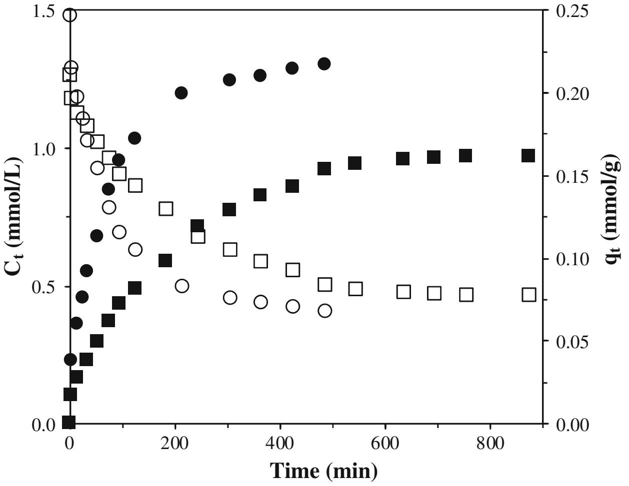


Fig. 4 Desorption kinetics for saturated resin MN-202 with (*filled circle*, *open circle*) benzene and (*filled square*, *open square*) toluene using a 50 % methanol solution: *open symbols* q_t (mmol/g); *solid symbols* C_t (mmol/L)

In order to provide a quantitative description of the adsorption process dynamics, a mass transfer model was developed based on the following assumptions (Vilar et al. 2007, 2008): the effect of the external film diffusion on the adsorption rate is negligible when applying adequate stirring; the sorption rate is controlled by the linear driving force model (LDF); the adsorption process is isothermal and there is equilibrium between the bound and dissolved BTX compounds, as formulated by the Langmuir isotherm; and the particles are spherical.

Mass conservation inside the particles

$$\frac{\partial x(r,t)}{\partial t} = \frac{1}{\tau_d}\left[\frac{\partial^2 x(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial x(r,t)}{\partial r}\right]; \ \tau_d = \frac{R_0^2}{D_h} \tag{9}$$

where $x(r,t)$ is the dimensionless BTX concentrations in solid phase, t is time, r is the dimensionless radial coordinate inside the particle, τ_d is the time constant for diffusion of BTX compounds into the particle (min), D_h is the homogeneous diffusion coefficient inside the particle (cm^2/s), and R_0 is the radius of the adsorbent particles (cm).

If the average BTX concentration inside the particle is considered, instead of a concentration profile, the following equations are obtained:

Kinetic law:

$$\frac{d\langle x(t)\rangle}{dt} = k_p a_p[x^*(t) - \langle x(t)\rangle];\; k_p a_p = \frac{D_h}{\phi R_0^2} = \frac{15}{\tau_d};$$

$$\phi = \frac{1}{15};\; a_p = \frac{3}{R_0} \tag{10}$$

where $\langle x(t)\rangle$ is the dimensionless average BTX concentration inside the particle, $x^*(t)$ the dimensionless BTX concentration in the solid phase, given by the equilibrium law, k_p is the mass transfer coefficient for intraparticle diffusion (cm/s) and a_p is the specific area of the spherical particles (1/cm).

Mass conservation in the fluid inside the closed vessel:

$$\langle x(t)\rangle = \frac{1}{\xi}(1 - x_b(t)) \tag{11}$$

Initial condition:

$$t = 0,\; x_b(t) = 1,\; \langle x(t)\rangle = 0 \tag{12}$$

Dimensionless variables:

$$x_b(t) = \frac{C_b(t)}{C_{b_0}};\; x(r,t) = \frac{q(R,t)}{q_L};\; \langle x(t)\rangle = \frac{\langle q(t)\rangle}{q_L};$$

$$r = \frac{R}{R_0};\; x^*(t) = \frac{q_{BTX}(t)}{q_L};\; \xi = \frac{Wq_L}{VC_{b_0}}$$

where V is the BTX solution volume (L), W the mass of adsorbent (g), $C_b(t)$ and $\langle q(t)\rangle$ the concentration of BTX compounds in the liquid phase (mmol BTX/L) and the average BTX concentration in the solid phase (mmol BTX/g biosorbent), respectively, R the radial position in the particle (cm), C_{b_0} the initial BTX concentration in the liquid phase (mmol BTX/L), $x_b(t)$ the dimensionless BTX concentrations in liquid and ξ the batch capacity factor (dimensionless).

Rearranging Eqs. 10 and 11 the following expression is obtained, which can be solved analytically using the initial conditions of Eq. 12:

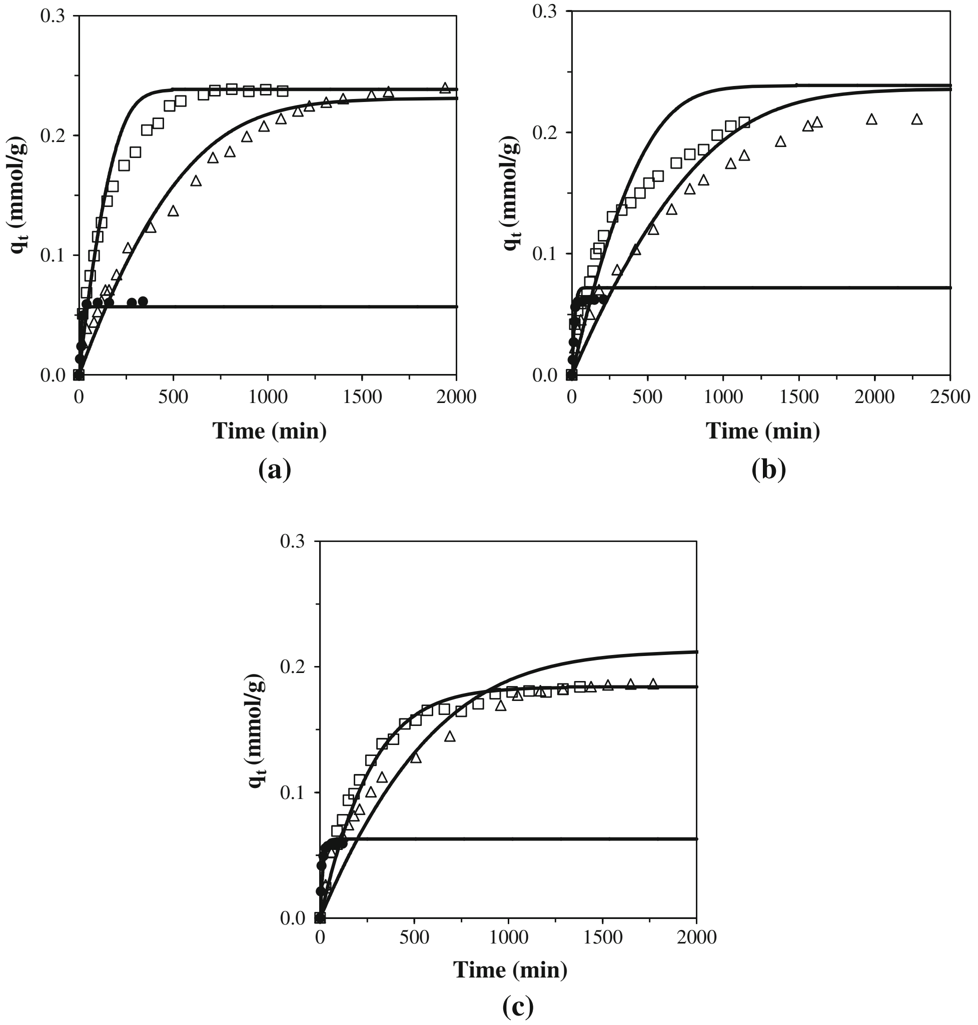


Fig. 5 Evolution of concentration **a** benzene, **b** toluene and **c** *o*-xylene adsorbed on different adsorbents with contact time: experimental data and predicted profiles using a linear driving force model. *Square* CD 500, *triangle* MN-202, *circle* Claytone-40, *horizontal bar* kinetic model LDF

Table 5 Estimated parameters for the mass transfer model

Adsorbent	Adsorbate	$k_p \times a_p$ (1/min)	τ_d (min)	D_h (cm^2/s)
CD 500	Benzene	2.5×10^{-3}	6.0×10^{3}	3.6×10^{-9}
	Toluene	1.0×10^{-3}	1.5×10^{4}	1.4×10^{-9}
	o-Xylene	2.0×10^{-3}	7.5×10^{3}	2.9×10^{-9}
MN-202	Benzene	7.0×10^{-4}	2.1×10^{4}	5.6×10^{-10}
	Toluene	5.0×10^{-4}	3.0×10^{4}	4.0×10^{-10}
	o-Xylene	9.0×10^{-4}	1.7×10^{4}	7.2×10^{-10}
Claytone-40	Benzene	5.5×10^{-2}	2.7×10^{2}	8.4×10^{-10}
	Toluene	2.5×10^{-2}	6.0×10^{2}	3.8×10^{-10}
	o-Xylene	4.0×10^{-2}	3.8×10^{2}	6.1×10^{-10}

$$\frac{1}{k_p a_p}\frac{dx_b(t)}{dt} + \left(\frac{\xi K_L C_{b_0}}{1 + K_L C_{b_0} x_b(t)} + 1\right) x_b(t) = 1 \qquad (13)$$

Figure 5 shows the evolution of experimental and estimated BTX concentration during the adsorption onto the three tested adsorbents with contact time. Although the mass transfer model fits reasonably the experimental data, for the polymeric resin, pore diffusion controls the process and the LDF approximation can't predict well the experimental data. Table 5 presents the estimated parameters for the mass transfer model.

D_h values are lower than the molecular diffusivity of benzene, toluene and *o*-xylene in water ($D_{\text{benzene}} = 1.09 \times 10^{-5}$ cm^2/s, $D_{\text{toluene}} = 0.915 \times 10^{-5}$ cm^2/s, $D_{o\text{-xylene}} = 0.569 \times 10^{-5}$ cm^2/s) (Price and Söderman 2000; Gustafson and Dickhut 1994), suggesting that a resistance to the diffusion process exists.

4 Conclusions

BTX compounds removal from aqueous solutions was successfully achieved using two alternative adsorbents, a polymeric resin MN-202 and Claytone-40, and adsorption capacities were compared with the activated carbon CD 500. The MN-202 resin has a similar BTX adsorption capacity to the activated carbon CD 500, and more than four times higher than for the Claytone-40. Although the adsorption capacity of each adsorbent is similar for benzene, toluene and *o*-xylene, the BTX compounds have a different affinity to each adsorbent, increasing in the following order benzene < toluene < *o*-xylene.

The adsorption kinetics of BTX compounds is faster using the Claytone-40, followed by activated carbon CD 500 and resin MN-202, mainly associated to pore diffusion resistance. The equilibrium adsorption of BTX compounds was well described by the Langmuir model. Kinetics at batch system was modelled using a mass transfer kinetic model, considering that the sorption rate is controlled by a LDF, leading to homogeneous diffusivity coefficients, D_h, between 3.8×10^{-10} and 3.6×10^{-9} cm^2/s. In general, benzene diffuses faster than toluene and *o*-xylene, which is in agreement with molecular diffusivity in water. A 50 % methanol solution can be used as eluant, resulting in desorption efficiencies of 73 and 63 % for benzene and toluene respectively. Desorption kinetics for benzene (300 min) were faster than for toluene (600 min) indicating that toluene binds strongly to the resin, which is in agreement with the Langmuir affinity constant values (K_L).

Polymeric resins show great promise as BTX sorbent candidates in aqueous applications due to its high specific surface area and porosity, similar to activated carbon, being possible to be reused in different consecutive adsorption/desorption cycles.

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