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Removal of an emerging pharmaceutical compound by adsorption in fixed bed column

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ABSTRACT

Adsorption of atenolol on granular activated carbon in a fixed bed column was investigated. This micropollutant was effectively adsorbed onto the activated carbon; therefore, the effect of some operation parameters on the performance of the breakthrough curve was studied. Some adsorption parameters, as the adsorption capacities at breakthrough and saturation time, the length of the mass transfer zone (mtz) and the fractional bed utilization were estimated. Four kinetic models, including Adams–Bohart, Wolborska, Thomas, and Yoon–Nelson model, were used to determine the adsorption parameters and to predict the breakthrough curves. Among all examined models, Thomas and Yoon–Nelson were found to be the most suitable for simulation of the breakthrough curve of atenolol uptake on granular activated carbon fixed bed column.

Keywords: Adsorption; Atenolol; Wastewater; Emerging contaminant; Mathematical model; Fixed bed column.

1. Introduction

Emerging pollutants are defined as substances that were previously undetected or had not been considered as a risk [1]. The main sources of non-regulated contaminants in the environment are wastewater treatment plant effluents [2], which are not designed to eliminate these compounds completely. They are present in treated wastewaters at trace levels (μg l^{-1} to ng l^{-1}), and include personal care products, pharmaceuticals, surfactants, flame retardants, industrial chemicals, gasoline additives, disinfection byproducts, etc. These contaminants do not need to be persistent in the environment to cause deleterious effects, since their high transformation and removal rates can be offset by their continuous introduction into the environment. Among the various substances that can be categorized as emerging pollutants, pharmaceutical compounds (PCs) are of special concern because of the volumes introduced to the environment, their endocrine disrupting activity, and a potential increase of bacterial resistance [3].

In this sense, it is estimated that hundreds of tons of PCs are produced and consumed in developed countries each year [4–6]. Most of them end up being excreted completely unchanged or only slightly transformed to polar molecules. Some of these compounds are easily removed and degraded during sewage treatment, mainly by adsorption and bio-degradation; however, they can still be detected at μg l^{-1} levels in treated effluents and receiving waters.

On the other hand, the health effects of the consumption of PCs at low concentration levels are not fully

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understood [7,8], and it hasn't been determined yet if levels of these compounds found in drinking water pose a human health risk [1]. Some research indicate that the low concentrations of PCs and other contaminants present in drinking water are not harmful to humans from a toxicological point of view, but their presence is still not desirable as a precautionary principle [9].

As a means to treat PCs, adsorption has achieved prominence for its being efficient even at low pollutant concentration levels. In this case, the adsorption process is an efficient technology to remove organic substances from aqueous streams. For this reason, activated carbon adsorption has been applied for the last several decades. In general, fixed-bed adsorbers have been used for wastewater treatments.

The compound used in this work is atenolol, a β-adrenoreceptor blocking agent, which is used as an antihypertensive drug. β-Blockers are exceptionally toxic and have a narrow therapeutic range. Its presence was reported in groundwater at concentrations up to μg l^{-1} [10–12].

Studies about the atenolol treatment by adsorption in fixed bed are low. In this work we have studied the removal of atenolol in water by activated carbon in fixed bed column operation. To our knowledge, this is one of the first studies on the elimination of atenolol by activated carbon fixed bed. In the present study, the effect of various operating variables as inlet adsorbate concentration, flow rate and bed length on the process is studied. Several empirical models have been applied to predict the dynamic column adsorption, as Bohart–Adams, Thomas, Wolborska and Yoon–Nelson.

2. Materials and methods

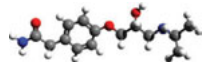
2.1. Adsorbent material

Granular activated carbon (Filtrasorb 400) was used in this study (supplied by Calgon, France). Before use, the adsorbent was washed with water to remove surface impurities, followed by drying at 100°C for 48 h. The size fraction between 0.5 and 0.589 mm was selected by sieving (ρ_P = 453.6 g l^{-1}, ε_P = 0.410).

2.2. Pharmaceutical compound

Atenolol was purchased from Sigma-Aldrich (Steinheim, Germany), in analytical purity and used in the experiments directly without any further purification. Solutions of atenolol of appropriate concentration were prepared by diluting a stock solution. The main characteristics of atenolol used in this work and the structure are shown in Table 1.

Table 1
Main characteristics of atenolol

Structure	
Category	β-Blocker
CAS number	29122-68-7
Molecular weight (g mol^{-1})	266.34
Log K_{ow}	0.16
*pK*a	9.43
Water solubility (mg l^{-1})	13300
Molecular formulae	$C_{14}H_{22}N_2O_3$
Size (Å)	4.8

2.3. Analytical techniques

All analyses were carried out by High Pressure Liquid Cromatography using a chromatograph Varian ProStar 230 equipped with a UV–vis PDA detector under the following conditions: Mediterranea column C18 (4.6 mm i.d. × 250 mm., 5 μm particle size), 100 μl aliquots were injected into the chromatograph. The isocratic mobile phase was a 20:80 (v/v) acetonitrile/phosphate buffer solution (pH 7) at a flow rate of 1.0 ml min^{-1}. Due to low concentrations that exhibit these contaminants in natural and wastewaters (at μg l^{-1} level), previous to analysis it was necessary to preconcentrate the samples by solid-phase extraction (SPE) which was performed on a SEP Oasis C18 Waters cartridge (60 mg, 3 cm^3). Oasis HLB cartridges (3 cm^3, 60 mg) were used as received. The cartridges were placed on a vacuum manifold and the vacuum pressure was adjusted to achieve the required flow rate. The cartridges were conditioned successively.

2.4. Characterization of adsorbent

Textural characterization of activated carbon was done by using N_2 adsorption–desorption at 77 K in a Micromeritics ASAP 2010 apparatus, and mercury intrusion porosimetry in a Thermo Finnigan Pascal 140–440. Thermogravimetric analysis (TGA) experiments were performed with a heating rate of 10°C min^{-1} in inert atmosphere on a Seiko EXSTAR 6000 TGA Instrument, from 20°C to 900°C, at an helium flow rate of 30 ml min^{-1}. Detailed results for the solid characterization can be consulted elsewhere [13,14].

2.5. Adsorption experiments

Batch equilibrium experiments were conducted using conical flasks (250 ml) immersed in a thermostatic bath at 25°C ± 1°C. The suspensions containing different

doses of activated carbon and the solutions of atenolol were shaken with a magnetic stirrer at constant temperature to reach equilibrium.

The equilibrium concentrations of each solution were determined. The amount of atenolol adsorbed on activated carbon was determined by the difference between the initial and remaining at equilibrium time concentrations in solution. The amount of adsorbed atenolol at equilibrium, q_{eq} (mg g^{-1}) was calculated by the next expression:

$$q_{eq} = \frac{(C_0 - C_{eq})V}{W} \quad (1)$$

where C_o and C_{eq} (mg l^{-1}) are the liquid-phase initial and equilibrium concentrations of atenolol, respectively. V is the volume of the solution (l), and W is the mass of adsorbent (g). The adsorption of atenolol on the activated carbon was also evaluated at constant temperature of 30°C for the adsorption isotherms.

Fixed bed experiments were conducted using borosilicate glass columns of 6 mm i.d. and 30 cm length. The column was packed with the granular activated carbon and then, filled with a layer of glass balls (1 mm in diameter) to compact the mass of adsorbent and to avoid dead volumes. The influent to the column was pumped using a Dinko multichannel peristaltic pump, model D25V.

Atenolol solutions with concentration in the range of 100–500 μg l^{-1} and volumetric flow rate in the range of 1.5–3.0 ml min^{-1} were passed in the down-flow mode through the bed. The effluent was collected at time intervals and its concentration was determined by HPLC.

All experiments were performed at 25°C ± 1°C using ultrapure water at the pH value of the solution itself. Table 2 summarizes the operating conditions for each set of experiments, modifying the following parameters: initial influent concentration, flow rate and weight of adsorbent or bed depth.

Table 2
Operation conditions in fixed bed column experiments

	Column length (cm)	Initial concentration (μg l^{-1})	Volumetric flow rate (ml min^{-1})
Different initial concentration	2.0	300.0	1.5
	2.0	500.0	1.5
Different volumetric flow rates	2.0	100.0	2.0
	2.0	100.0	3.0
Different column lengths	1.0	100.0	1.5
	2.0	100.0	1.5
	3.0	100.0	1.5

3. Results and discussion

3.1. Characterization of granular activated carbon

The properties of granular activated carbon determined in this study are listed in Table 3. This material exhibited a narrow pore size distribution and was essentially microporous. On the other hand, the TGA shows two stages the dehydration and the active pyrolysis, respectively. The weight loss started around 475–500°C and continued to 900°, probably related to the decomposition of more stable surface oxygen groups such as ketones, ethers and hydroxyls originally present in the structure of the granular activated carbon [13]. Also, the point of zero charge, $pH_{PZC,}$ of this material was obtained. The results indicated that the pH_{PZC} was 7.6.

3.2. Batch adsorption experiments

For atenolol, the equilibrium state was considered reached after about 25 h, since the variations in equilibrium adsorption capacity did not change more than 5% (Fig. 1).

Table 3
Physicochemical properties of the granular activated carbon F-400

Parameters	Value
Surface area (m^2 g^{-1})	384.0
S_{BET} (m^2 g^{-1})	997.0
Micropore volume (cm^3 g^{-1})	0.26
pH_{PZC}	7.6
Basicity (μeq g^{-1})	462.0
Acidity (μeq g^{-1})	802.0

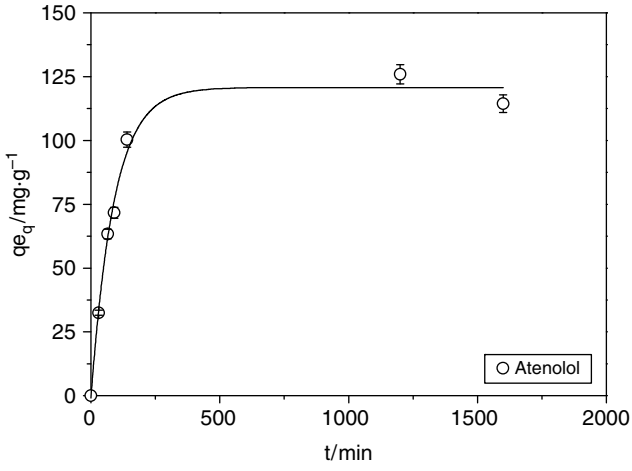


Fig. 1. Equilibrium time for atenolol.

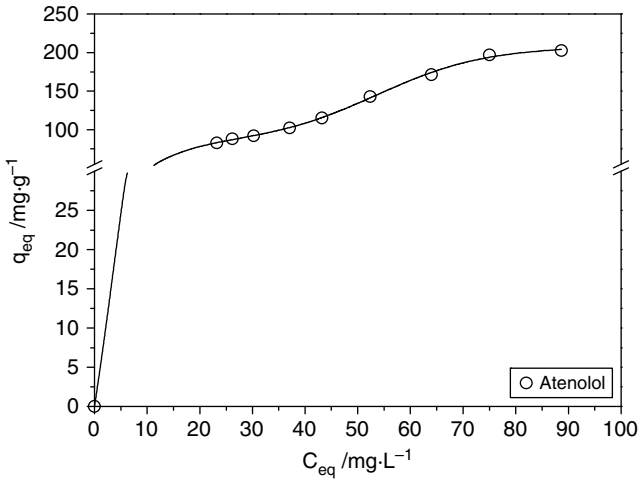


Fig. 2. Adsorption isotherm of atenolol.

Therefore, the equilibrium adsorption capacity of the atenolol on the granular activated carbon versus the concentration of the aqueous solution at equilibrium is given in Fig. 2. The shape of the isotherm shows that it corresponds to type L3; the systems with this type of isotherms are indicative of a high affinity between the adsorbate and the adsorbent for low concentrations, which decreases as the concentration increases. These isotherms are characterized by a decrease in the slope of the curve with increasing the concentration of adsorbate in the solution, due to a decrease of the available adsorption sites.

BET model adsorption is used to describe this isotherm. This equation fit correctly the experimental isotherm data of the granular activated carbon. The estimated model BET parameters and the correlation coefficient are reported in Table 4.

3.3. Fixed bed adsorption experiments

In the set of experiments reported in Table 2, the influence of the initial atenolol concentration, the flow rate, and the column length on the performance of the breakthrough curves were evaluated.

Table 4
BET model parameters related to the adsorption isotherm of atenolol

Parameters	Value
q_{sat}	80.4
K	16.7
C_0	115.0
R^2	0.9962

3.3.1. Effect of the inlet atenolol concentration

The adsorption performance of activated carbon fixed bed was tested at various atenolol inlet concentrations. The breakthrough curves were obtained by changing initial atenolol concentration from 300 to 500 μg l^{-1} at 1.5 ml min^{-1} of flow rate and a length of bed of 2.0 cm (Fig. 3a).

As expected, a decrease in the inlet concentration leads to an increase in the breakthrough time, as the binding sites became more slowly saturated in the system. Besides, a decrease in the initial concentration gave a slightly lower slope of the curve, which indicates a slower transport due to a decreased diffusion coefficient or decreased mass transfer coefficient. Breakthrough (at C/C_0 = 0.25) occurred after 51.0 h at 300 μg l^{-1} inlet atenolol concentration while as breakthrough time appeared after 10.5 h at an initial atenolol concentration of 500 μg l^{-1}.

3.3.2. Effect of the flow rate

In the removal studies in the continuous-flow fixed column, the flow rate was changed from 2.0 to 3.0 ml min^{-1} while the atenolol concentration in the feed was held constant at 100 μg l^{-1}, being the bed depth of 2.0 cm. The breakthrough curves at different flow rates are given in Fig. 3b. As can be seen in this figure, at the higher flow rate of 3.0 ml min^{-1}, a decrease of the breakthrough time was observed. This behaviour can be explained that atenolol adsorption is affected by insufficient or limited residence time of the adsorbate in the column, the diffusion of the adsorbate into the pores of the adsorbent and limited number of active sites for the adsorption process [15]. In this case, it can be observed that the breakthrough curve obtained at the higher flow rate, 3.0 ml min^{-1}, presents a higher slope, which indicates a decrease in the mass transfer resistance of the process. Breakthrough (C/C_0 = 0.15) occurred after 171.6 h at 2.0 ml min^{-1} of flow rate, and after 123.8 h at flow rate of 3.0 ml min^{-1}.

3.3.3. Effect of the column length

The breakthrough curves were examined at different column lengths, from 1.0 to 3.0 cm, being held constant the initial concentration at 100 μg l^{-1} and the flow rate at 1.5 ml min^{-1}. The results were shown in Fig. 3c. It can be seen, as expected, that the higher bed length, 3.0 cm, leads to the higher breakthrough time, being this parameter lower when the column length is 1.0 and 2.0 cm. As to slopes of the breakthrough curves, it can be observed that they are roughly similar, as a change of the column length, at same conditions of concentration and flow rate, does not affect the mass transfer of the process. The difference between the slopes which is observed in Fig. 3c,

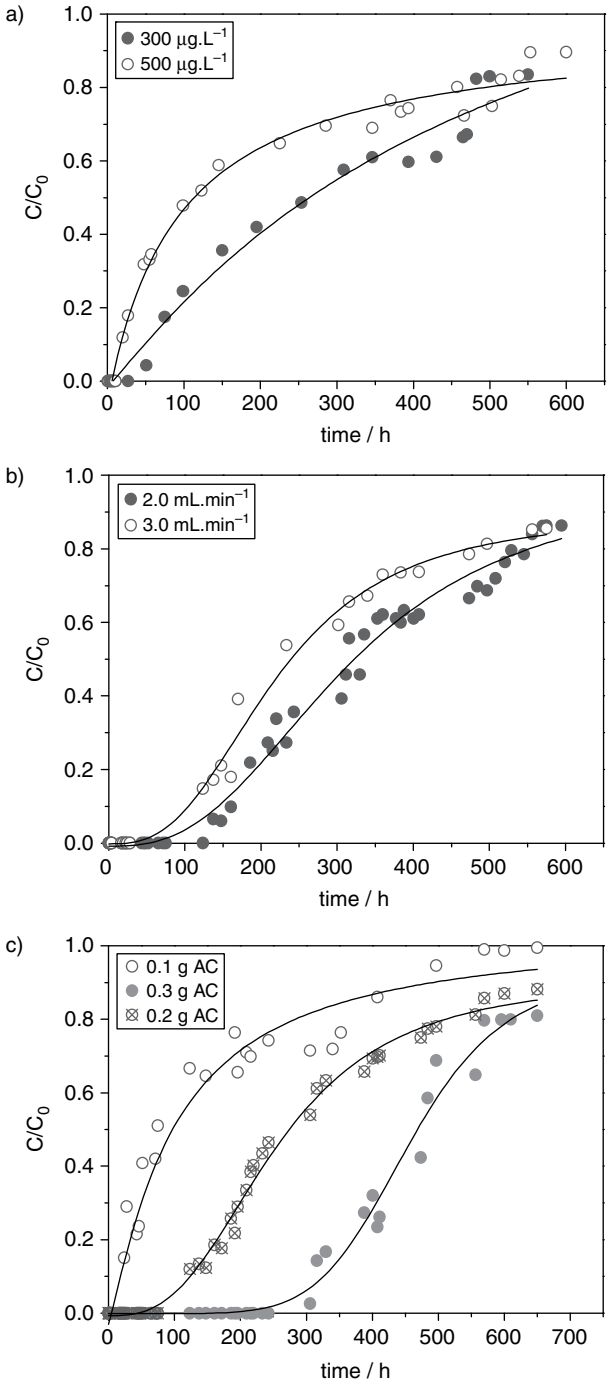


Fig. 3. Breakthrough curves of atenolol removal by granular activated carbon fixed bed columns of: (a) Different inlet atenolol concentrations (column length = 2.0 cm, flow rate = 1.5 ml.min^{-1}). (b) Different volumetric flow rates (column length = 2.0 cm, initial conc. = 100 µg.l^{-1}). (c) Different column lengths (inlet atenolol conc. = 100 µg.l^{-1}, flow rate = 1.5 mL.min^{-1}).

can be attributed to, at this column lengths, the front of the concentration in the bed is not fully developed [16]. Breakthrough (C/C_0 = 0.15) occurred after 24.3 h at 1.0 cm of bed length, 153.4 h at 2.0 cm of column length and 316.0 h at a column length of 3.0 cm.

3.3.4. Adsorption parameters estimation

In general, it can be observed that the operational conditions (initial atenolol concentration, flow rate and column length) of the bed influence on the mass transfer process and therefore, change the adsorption capacities, mass transfer zone (MTZ) and bed utilization values. Different parameters, such as adsorption capacities at breakthrough time (q_r) and at saturation time (q_s), length of the MTZ and fractional bed utilization (FBU) of the process are reported in Table 5.

As can be observed in Table 5, an increase in the column length leads to a slight variation in the length of the MTZ. These values should be constant, therefore the column lengths tested are not high enough to have a fully developed profile, as mentioned above. MTZ values were calculated by the next expression [17]:

$$\mathrm{MTZ} = Z \cdot \left(1 - \frac{q_r}{q_s}\right) \quad (2)$$

where, q_r is the adsorption capacity at breakthrough time (mg g^{-1}), q_s, the adsorption capacity at saturation time (mg g^{-1}) and Z is the bed length (cm). This expression is applied generally in systems with higher column lengths, which indicates that a fully developed bed has been achieved.

It can be seen that an increase of the initial atenolol concentration (500 µg l^{-1}) leads to a worse fractional bed utilization and to the highest adsorption capacity at saturation time (q_s), 24.96 mg g^{-1}, which is very near to the equilibrium adsorption capacity predicted by the isotherm curve at this concentration. The driving force for adsorption is the concentration difference between the adsorbate on the adsorbent and the adsorbate in the solution. A high concentration difference provides a high driving force for the adsorption process and this may explain why higher adsorption capacities were achieved in the column with a higher atenolol concentration [15].

3.3.5. Modelling of the breakthrough curves

3.3.5.1. The Adams–Bohart model The fundamental equations describing the relationship between C/C_0 and t in a flowing system were established by Adams and Bohart [18] for the adsorption of chlorine on charcoal. Although the original work by Adams–Bohart was done for the gas-charcoal adsorption system, its overall approach can be applied successfully in quantitative description of other systems. This model assumes that the adsorption rate is proportional to both the residual

Table 5
Adsorption capacities (q_r, q_s), MTZ and FBU values of atenolol

Parameter	Column length (cm)			Initial concentration (μg l^{-1})		Volumetric flow rate (ml min^{-1})	
	1.0	2.0	3.0	300.0	500.0	2.0	3.0
q_r (mg g^{-1})	1.85	5.30	7.63	4.28	1.42	8.64	8.88
q_s (mg g^{-1})	6.95	9.38	10.64	24.81	24.96	16.29	17.91
MTZ (cm)	0.75	0.87	0.85	1.65	1.89	0.94	1.00
FBU	0.25	0.57	0.72	0.17	0.06	0.53	0.50

capacity of the adsorbent and the concentration of the adsorbate. So, in general, the Adams–Bohart model is used for the description of the initial part of the breakthrough curve [15]. Hutchins linearized the Bohart–Adams equations to give bed depth service time (BDST) plot between time and Z [19]:

$$t = \frac{N_0}{C_0 \cdot U} \cdot Z - \frac{1}{C_0 \cdot k_{AB}} \ln\left(\frac{C_0}{C_B} - 1\right) \quad (3)$$

where C_0 is the initial concentration of atenolol (mg l^{-1}), C_B is the desired concentration of adsorbate at breakthrough time (C_B/C_0 = 0.15 for atenolol, in this case), k_{AB} is the adsorption rate constant (l mg^{-1} h^{-1}), N_0 is the adsorption capacity of the system (mg l^{-1}), Z is the bed length (cm), U is the linear flow velocity (cm h^{-1}) and t is the service time of column under above conditions (h).

Eq. (3) can be defined by the next parameters:

$$a = \text{slope} = \frac{N_0}{C_0 \cdot U} \quad (4)$$

$$b = \text{intercept} = \frac{1}{C_0 \cdot k_{AB}} \cdot \ln\left(\frac{C_0}{C_B} - 1\right) \quad (5)$$

In the Fig. 4, it can be seen the plot of column length, Z (cm) versus time, *t* (h) for 15% and 81% saturation of bed. The equations obtained are these:

For 81% saturation:

$$t = 135.4x + 257.7 \quad (6)$$

For 15% saturation:

$$t = 145.9x - 127.1 \quad (7)$$

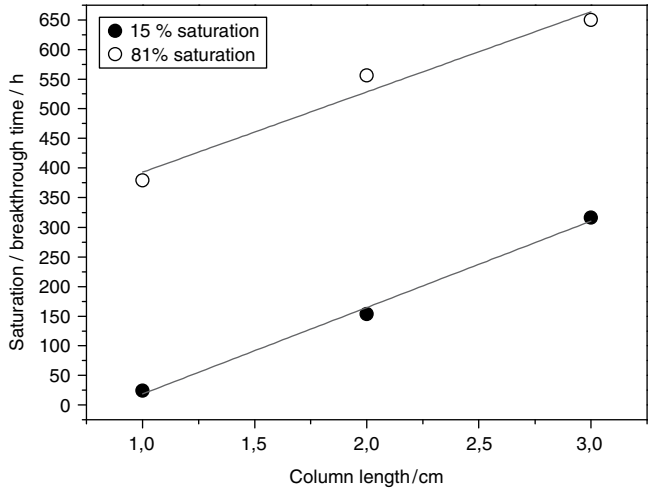


Fig. 4. Time for saturation compared to column length for atenolol adsorption on GAC fixed bed columns according to Bohart and Adams model.

In general, a plot between *t* and *Z* must result in a straight line passing through the origin, however, in both cases, the lines do not pass through the origin. This behavior indicates that the adsorption of atenolol on activated carbon occurs through complex mechanism, and more than one rate limiting step are involved in the adsorption process [19]. Therefore, the horizontal distance between the straight lines is called the height of exchange zone, namely, the MTZ [20]. The MTZ value obtained for this case is 2.5 cm, and therefore, it was found an average value of this parameter of 0.82 cm. The difference between these values can be explained through two aspects. One of them is that the experimental depths used are not high enough to ensure a fully developed profile of the bed, which generates a variation on the MTZ values, which should be roughly constant, as mentioned in Section 3.3.4. Also, adsorption of atenolol on activated carbon occurs through complex mechanism, as mentioned above. So, it indicates that a simplified model as Bohart and Adams, is not suitable to define complex adsorption mechanisms, as caffeine on activated carbon.

From the slope and intercept of the 15% saturation line, design parameters like N_0 and k_{AB} could be estimated using Eqs. (6) and (7), respectively. The values of k_{AB} and N_0 were found to be 0.136 l mg^{-1} h^{-1} and 10.24 mg g^{-1}, this late, similar to the values shown in Table 5.

3.3.5.2. The Wolborska model Wolborska [21] gave a relationship describing the concentration distribution in the bed for the low concentration region of the breakthrough curve, as occurs in Bohart and Adams model. β, a constant in Wolborska model, is an effective coefficient which reflects the effect the mass transfer in the liquid phase and the axial dispersion [19]. Wolborska observed that for low Z or and high Q values, the axial diffusion is negligible and $\beta = \beta_0$, the external mass transfer coefficient. This model used the next linearized expression:

$$\ln \frac{C}{C_0} = \frac{\beta \cdot C_0}{N_0} \cdot t - \frac{\beta \cdot Z}{U} \tag{8}$$

where C_0 is the initial concentration of atenolol (mg l^{-1}), N_0 is the adsorption capacity (mg l^{-1}), ß is the kinetic coefficient of the external mass transfer (h^{-1}), Z is the bed length (cm) and U is the linear flow velocity (cm h^{-1}).

In this case, after applying Eq. (8) and the not linearized expression of Eq. (8) to the experimental data for varying inlet atenolol concentration, flow rate and column length, it could not be obtained a good linear relationship between $\ln C/C_0$ and t, even in the region below to 50% saturation; for all breakthrough curves ($R^2 < 0.6$).

3.3.5.3. The Thomas model Succesful design of a column adsorption processes requires prediction of the concentration–time profile or namely, the breakthrough curve for the system adsorbate–adsorbent [15]. Traditionally, the Thomas model has been used to fulfil this purpose. The Thomas or reaction model [22], which assumes Langmuir kinetics of adsorption–desorption and no axial diffusion is derived with the adsorption that the rate driving force obeys second-order reversible reaction kinetics. The primary weakness of the Thomas solution is that its derivation is based on second order reaction kinetics. Adsorption is usually not limited by chemical reaction kinetics but is often controlled by interphase mass transfer. This discrepancy can lead to some error when this method is applied to model the adsorption process [15]. The linearized expression of the model has the following form:

$$\ln\left(\frac{C}{C_0} - 1\right) = \frac{k_T \cdot q_0 \cdot m}{Q} - k_T \cdot C_0 \cdot t \tag{9}$$

where C_0 is the initial concentration of atenolol (mg l^{-1}), q_0 is the adsorption capacity of the system atenolol-activated carbon (mg l^{-1}), k_T is the Thomas rate constant (l h^{-1} mg^{-1}), m is the mass of the adsorbent in the column (g) and Q is the volumetric flow rate (l h^{-1}).

Thomas model parameters, k_T and $q_{0,}$ were determined by not linearized expression of Eq. (8) and are shown in Table 6. Therefore, adsorption capacity (q_0) values calculated by this model were compared with experimental data using standard error of estimate (SE) method, with this expression:

$$SE = \sqrt{\sum \frac{\left(q_{0(exp)} - q_{0(cal)}\right)^2}{N}} \tag{10}$$

The estimation of error between the experimental and predicted values of C/C_0 was done by using modified form of the Marquardt's percent standard deviation (MPSD) represented by next equation in Table 6:

$$MPSD = 100 \cdot \sqrt{\frac{1}{N-P}\sum_{i=1}^{n}\left(\frac{(C/C_0)_{exp} - (C/C_0)_{cal}}{(C/C_0)_{exp}}\right)_i^2} \tag{11}$$

As expected (Table 5), it can be observed from Table 6 that the values of q_0 increased with an increase in the value of C_0 and the volumetric flow rate.

Table 6
Predicted parameters for Thomas model and model deviations for atenolol adsorption on GAC

Z (cm)	C_0 (µg l^{-1})	Q (ml.min^{-1})	k_T (l h^{-1} mg^{-1})	$q_{0\ exp}$ (mg g^{-1})	$q_{0\ cal}$ (mg g^{-1})	SE	MPSD
1.0	100.0	1.5	0.128	6.95	13.92	1.32	38.53
2.0	100.0	1.5	0.098	9.38	13.83	0.66	46.21
3.0	100.0	1.5	0.137	10.64	14.36	0.57	61.08
2.0	100.0	2.0	0.089	16.29	20.41	0.58	61.66
2.0	100.0	3.0	0.085	17.91	28.23	2.06	46.48
2.0	300.0	1.5	0.027	24.81	44.36	3.83	49.72
2.0	500.0	1.5	0.015	24.96	51.10	4.77	36.44

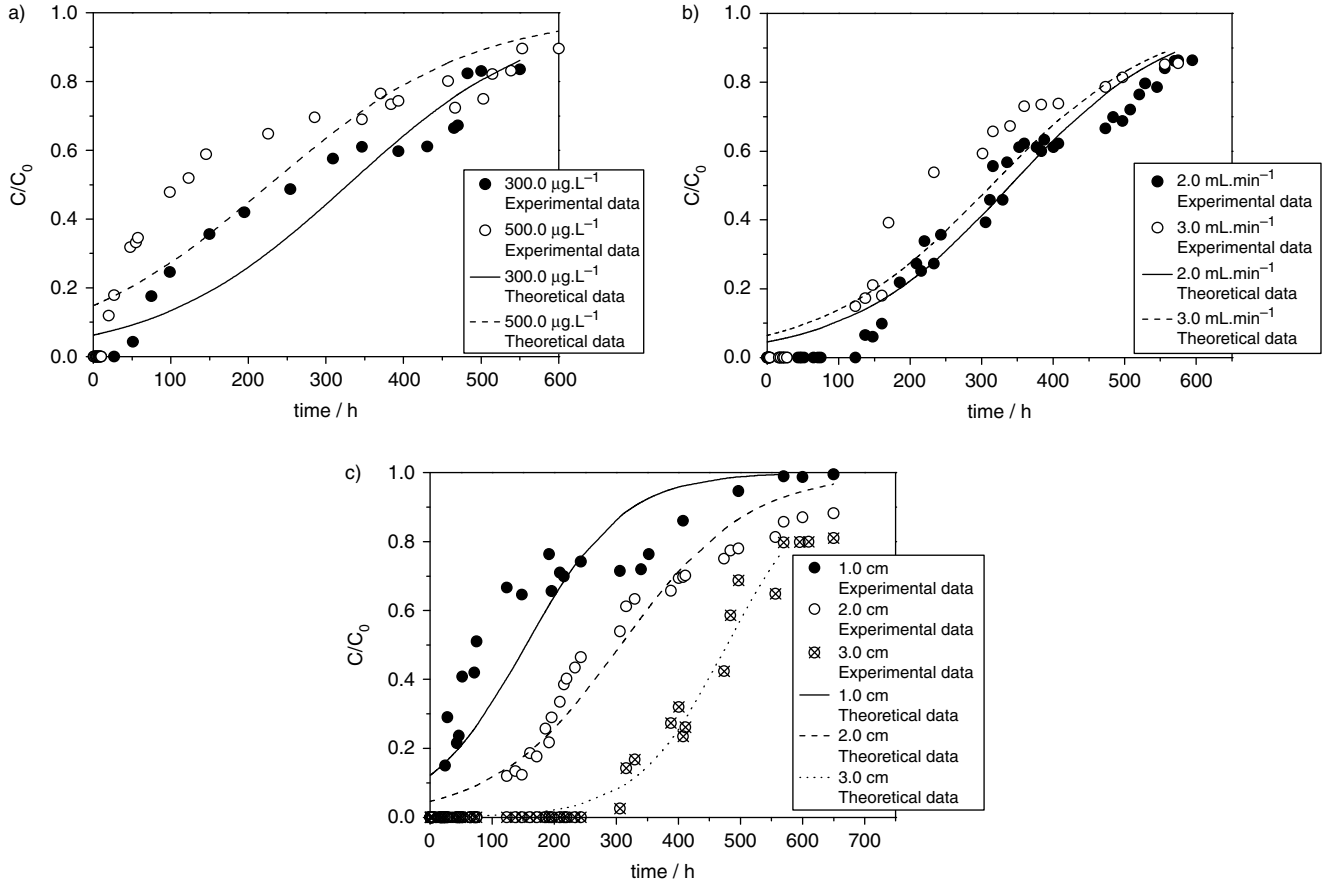


Fig. 5. Experimental and predicted breakthrough curves of atenolol removal by granular activated carbon fixed bed columns predicted by Thomas model: (a) Different inlet atenolol concentrations (column length = 2.0 cm, flow rate = 1.5 ml.min^{-1}). (b) Different volumetric flow rates (column length = 2.0 cm, initial conc. = 100 µg.l^{-1}). (c) Different column lengths (inlet atenolol conc. = 100 µg.l-1, flow rate = 1.5 ml.min^{-1}).

In Figs. 5a–c it can be seen the experimental and predicted breakthrough curves of atenolol removal by granular activated carbon packed columns using the Thomas model.

3.3.5.4. The Yoon and Nelson model Yoon and Nelson [23] developed a relatively simple model addressing the adsorption and breakthrough of adsorbate vapors or gases with respect to activated charcoal. This model is based on the assumption that the rate of decrease in the probability of adsorption of adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent. The Yoon and Nelson model not only is less complicated than other models, but also requires no detailed data concerning the characteristics of the adsorbate and adsorbent and the physical properties of the adsorption bed [15,19]. The Yoon and Nelson equation regarding to a single-component system is expressed as:

$$\ln\left(\frac{C}{C_0 - C}\right) = k_{YN} \cdot t - \tau \cdot k_{YN} \tag{12}$$

where C_0 is the initial concentration of atenolol (mg l^{-1}), k_{YN} is the rate constant (h^{-1}) and τ is the time required for reach 50% adsorbate breakthrough (h).

The calculation of theoretical breakthrough curves requires the determination of the parameters k_{YN} and τ for atenolol, which are reported in Table 7. The SE method, used to evaluate the difference between predicted and experimental τ values, Eq. (10), and MPSD values are reported in Table 7.

Figs. 6a–c shows the experimental and theoretical breakthrough curves obtained at different inlet concentrations, flow rates and column lengths using the Yoon–Nelson model. Fig. 6 and the data reported in Table 7 indicated that the τ values predicted by the Yoon–Nelson model are relatively close to the experimental results.

Table 7
Predicted parameters for Yoon–Nelson model and model deviations for atenolol adsorption on GAC

Z (cm)	C_0 (μg l^{-1})	Q (ml min^{-1})	k_{YN} (h^{-1})	τ_{exp} (h)	τ_{cal} (h)	SE	MPSD
1.0	100.0	1.5	0.014	75.0	137.72	11.85	37.88
2.0	100.0	1.5	0.010	305.75	307.32	0.23	46.21
3.0	100.0	1.5	0.013	478.45	479.12	0.10	66.80
2.0	100.0	2.0	0.009	332.06	347.82	2.21	56.79
2.0	100.0	3.0	0.010	233.5	276.3	8.56	45.19
2.0	300.0	1.5	0.008	262.65	316.9	10.64	57.42
2.0	500.0	1.5	0.0077	123.0	227.09	19.00	36.44

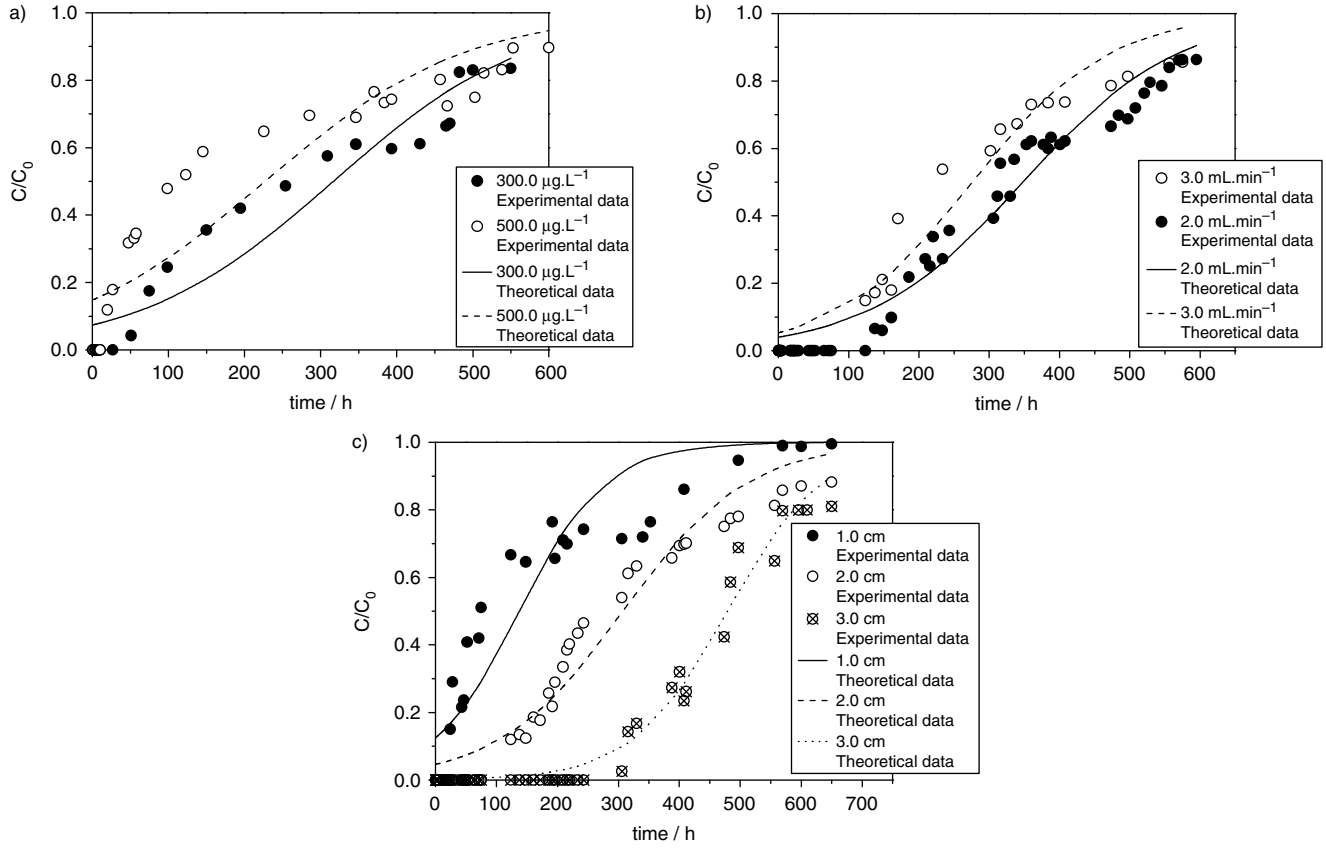


Fig. 6. Experimental and predicted breakthrough curves of atenolol removal by granular activated carbon fixed bed columns predicted by Yoon and Nelson model: (a) Different inlet atenolol concentrations (column length = 2.0 cm, flow rate = 1.5 ml.min^{-1}). (b) Different volumetric flow rates (column length = 2.0 cm, initial conc. = 100 μg.l^{-1}). (c) Different column lengths (inlet atenolol conc. = 100 μg.l^{-1}, flow rate = 1.5 ml.min^{-1}).

4. Conclusions

The present work illustrates that the adsorption of atenolol from aqueous solutions on a fixed bed of granular activated carbon is an interesting and effective treatment for the removal of this micropollutant, even at μg l^{-1} levels. It has been demonstrated that the shape of the breakthrough curves and the front of adsorption obtained is strongly dependent on operation parameters, as initial adsorbate concentration, volumetric flow rate and column length.

It is found that the breakthrough time decreases when inlet atenolol concentration and flow rate increase, and when column length decreases. Therefore, it has been shown that a variation in the initial concentration or the volumetric flow rate changed the slope of the breakthrough curve, so the mass transfer resistance of

the process is dependent on these parameters. Parameters as adsorption capacity at breakthrough time (q_r) and saturation time (q_s), length of the mass transfer zone (MTZ) and fractional bed utilization (FBU) were obtained for the named operation conditions.

The dynamic removal of atenolol can be described by empirical models as Bohart Adams, Wolborska, Thomas and Yoon–Nelson. Thomas and Yoon and Nelson models have been found more suitable for mathematical description of atenolol removal in fixed bed in the range studies.

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