REMOVAL OF PARACETAMOL ON BIOMASS-DERIVED ACTIVATED CARBON: MODELING THE FIXED BED BREAKTHROUGH CURVES USING BATCH ADSORPTION EXPERIMENTS

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Nomenclature (units used)

22 \( a \) empirical parameter \((\text{s}^{-1})\)

24 \( A_{\text{BET}} \) specific surface area by Brunauer, Emett, Teller method \((\text{m}^2 \text{g}^{-1})\)

25 \( A_{\text{DR}} \) Dubinin Radushkevich surface area \((\text{m}^2 \text{g}^{-1})\)

26 \( A_t \) external area \((\text{m}^2 \text{g}^{-1})\)

27 \( B \) time constant \((\text{s}^{-1})\)

28 \( b \) empirical parameter \((\text{m}^2 \text{s}^{-1})\)

29 \( c \) empirical parameter \((\text{s})\)

30 \( C \) outlet concentration \((\text{mg L}^{-1})\)

31 \( C_0 \) initial concentration \((\text{mg L}^{-1})\)

32 \( C_b \) paracetamol bed concentration \((\text{mol m}^{-3})\)

33 \( C_e \) equilibrium concentration \((\text{mg L}^{-1})\)

34 \( C_i \) inlet concentration \((\text{mg L}^{-1})\)

35 \( C_p \) concentration in the particle external surface \((\text{mol m}^{-3})\)

36 \( C_t \) concentration at time \( t \) \((\text{mg L}^{-1})\)

37 \( d \) empirical parameter \((\text{s})\)

38 \( D_e \) effective internal diffusion coefficient \((\text{m}^2 \text{s}^{-1})\)

39 \( D_l \) molecular diffusivity of the solute in water \((\text{m}^2 \text{s}^{-1})\)

40 \( D_s \) surface diffusion coefficient \((\text{m}^2 \text{s}^{-1})\)
$D_x$ axial dispersion coefficient (m$^2$s$^{-1}$)

$k_f$ external film mass-transfer coefficient (m s$^{-1}$)

$k_i$ intraparticle mass transfer (s$^{-1}$)

$K_L$ equilibrium constant of Langmuir equation (L mg$^{-1}$)

$K_{L0}$ pre-exponential factor in Langmuir equation (L mg$^{-1}$)

$L_b$ bed length (cm)

$N$ number of transfer units

$N_S$ diffusion molar flux (mol m$^{-2}$·s$^{-1}$)

$Q$ flow rate (mL min$^{-1}$)

$q$ mean concentration of solute adsorbed in the adsorbent particle

$q_{cal}$ calculated adsorption capacity from models at $C/C_i = 0.95$ (mg g$^{-1}$)

$q_{|C_p}$ adsorbed concentration at the solid external surface

$q_e$ adsorption capacity at equilibrium (mg g$^{-1}$)

$q_{exp}$ experimental adsorption capacity at $C/C_i \approx 0.95$ (mg g$^{-1}$)

$q_i$ adsorption capacity at $C_i$ concentration (mg g$^{-1}$)

$q_L$ maximum adsorption capacity at equilibrium of Langmuir equation (mg g$^{-1}$)

$q_m$ empirical parameter (mg g$^{-1}$)

$q_r$ adsorbed concentration at $r$ radial position in the particle (mol m$^{-3}$)

$q_{t}$ adsorption capacity at time $t$ (mg g$^{-1}$)
\( R \) gases constant (8.31 J mol\(^{-1}\)·K\(^{-1}\))

\( R_b \) bed radius (cm)

\( R_p \) particle size (mm)

\( R_S \) separation factor

\( r^2 \) determination coefficient

\( T \) throughput parameter

\( t \) time (min)

\( t_s \) stoichiometric time (min)

\( u \) superficial liquid velocity (m s\(^{-1}\))

\( V_b \) molar volume of solute at the normal boiling point (cm\(^3\) mol\(^{-1}\))

\( V_{DR} \) Dubinin Radushkevich narrow micropore volume (cm\(^2\) g\(^{-1}\))

\( V_{mes} \) mesopore volume from the N\(_2\) isotherm (cm\(^3\) g\(^{-1}\))

\( V_p \) total pore volume from the N\(_2\) isotherm (cm\(^3\) g\(^{-1}\))

\( V_t \) micropore volume from the N\(_2\) isotherm (cm\(^3\) g\(^{-1}\))

\( v_z \) axial velocity (m s\(^{-1}\))

\( w \) adsorbent dose (g L\(^{-1}\))

\( W \) mass of activated carbon (mg)

\( z \) axial position in bed
Greek characters

80 $\varepsilon_b$ bed porosity

81 $\varepsilon_p$ particle porosity

82 $\mu_l$ fluid dynamic viscosity (cP)

83 $\eta$ yield

84 $\rho_b$ bed density (kg m$^{-3}$)

85 $\rho_l$ fluid density (kg m$^{-3}$)

86 $\rho_p$ particle density (kg m$^{-3}$)
Abstract

The remediation of paracetamol (PA), an emerging contaminant frequently found in wastewater treatment plants, has been studied in the low concentration range (0.3-10 mg L$^{-1}$) using as adsorbent a biomass-derived activated carbon. PA uptake of up to 100 mg g$^{-1}$ over the activated carbon has been obtained, with the adsorption isotherms being fairly explained by the Langmuir model. The application of Reichemberg and the Vermeulen equations to the batch kinetics experiments allowed estimating homogeneous and heterogeneous diffusion coefficients, reflecting the dependence of diffusion with the surface coverage of PA. A series of rapid small-scale column tests were carried out to determine the breakthrough curves under different operational conditions (temperature, PA concentration, flow rate, bed length). The suitability of the proposed adsorbent for the remediation of PA in fixed-bed adsorption was proven by the high PA adsorption capacity along with the fast adsorption and the reduced height of the mass transfer zone of the columns. We have demonstrated that, thanks to the use of the heterogeneous diffusion coefficient, the proposed mathematical approach for the numerical solution to the mass balance of the column provides a reliable description of the breakthrough profiles and the design parameters, being much more accurate than models based in the classical linear driving force.

Keywords: Activated carbon, Adsorption, Paracetamol, Pharmaceuticals, Column adsorption, Modeling breakthrough curves
Highlights

• Activated carbon with well-developed porosity has been prepared from a biomass waste.

• It shows high removal efficiency of paracetamol in low concentrations (0.3-10 mg L\(^{-1}\)).

• Uptake of ca. 100 mg g\(^{-1}\) and narrow mass transfer zone is observed in fixed-bed adsorption.

• Heterogeneous diffusivity coefficient successfully describes the adsorption kinetics.

• Breakthrough curves are predicted using adsorption parameters of batch experiments.
1. Introduction

Pharmaceutical compounds are labeled as emerging environment pollutants because, as in the case of many other every-day use and personal care products, they are found in increasing amounts in urban and industrial wastewaters, and even in surface waters [1], [2] and [3]. Since these compounds have biological activity, there exist scientific and social concerns to control the impact of these micropollutants on the environmental systems. Although many of these compounds have been proved to be rather stable and can generate bioaccumulation and biomagnification processes, they do not need to persist in the environment to cause negative effects, since their elimination or transformation is compensated by daily continuous introduction, derived of discharges and elution from pharmaceutical production plants, hospitals, homes or landfills. It is possible to find a great number of studies that analyze their concentration in streams, rivers, ground, surface or drinking water. They report how efficiently the municipal wastewater plants are in their removal, providing consistent proofs of the low removal efficiency for broad groups of pharmaceutical compounds making necessary the implementation of additional wastewater treatments for their remediation [1], [4], [5] and [6]. More specifically, there are several works detailing the occurrence of pharmaceutical compounds in surface waters in concentrations that ranges from $10^{-9}$ to $10^{6}$ g L$^{-1}$. For instance, some studies realized in Spanish rivers, [7] and [8], showed the presence of a great variety of soluble pharmaceutical compounds.

The adsorption in fixed beds columns with activated carbon is one of the most efficient advanced methods to remove organic micropollutants from aqueous effluents. Activated carbon is broadly utilized in water and gas treatment due to its unmatched adsorption capacity and its competitive cost [9] and [10]. The removal efficiency of activated carbon are strongly dependent on tailoring its chemical and physical structure to match
the required properties for the application. On the one hand, the surface chemistry of the carbon should be to the least compatible for the adsorption of the pollutant in terms of polarity, acidity and aromatic degree. If adequately tuned, these properties can be profited for enhancing the removal efficiency of activated carbons [11], [12] and [13].

On the other hand, it is necessary to use adsorbents with a well-developed and reachable surface area, and reduced mass transfer limitations for enhancing the bed service time. In this sense, the accessibility to the micropores, which are responsible for most of the adsorption capacity of an activated carbon, can be enhanced by the presence of mesopores [14] and [15]. Thus, the adsorption equilibrium and kinetics for each specific contaminant are related to the chemical surface and the porous structure of the activated carbon used as adsorbent.

For envisaging the viability of activated carbons, it is critical to develop models and experimental procedures that could be used for accurately describing the dynamics of the pollutant adsorption and desorption under a variety of operating conditions from lab scale measurements. In this light, there has been considerable effort for determining these relationships using rapid small-scale column tests (RSSCT) [16]. These tests enable the design of fixed-bed activated carbon adsorbers in lab-scale that fairly reproduces the behavior of full-scale adsorbers [17], [18] and [19]. Even so, most of the laboratories are equipped for the determination of the thermodynamic and kinetic adsorption parameters using batch experiments, and the development of analytical tools for obtaining information of adsorbent performance in batch studies that would be relevant and valuable for predicting the removal performance of the adsorbents in fixed-bed adsorption is still necessary. The work herein aimed at conciliating removal performance as determined by batch and column experiments of a model organic micropollutant by a specifically made biomass-derived activated carbon, so that easy
and readily applicable protocols in batch configuration can be used to identify the adsorption isotherms and diffusion properties of carbons for column operation. The work herein details the removal of acetaminophen (paracetamol) at low concentrations (<10 mg L\(^{-1}\)) by adsorption on a biomass-based activated carbon in column operation. Paracetamol (PA) is an analgesic worldwide consumed and it is ubiquitously found in European surface waters [6] and [8], therefore being selected as a model emerging contaminant. Paracetamol adsorption in activated carbon have been widely studied during the last decade by Prof. Terzyk [20] and some other research groups [21], [22] and [23], although in concentrations much higher than those currently registered in wastewater treatment plants. As pointed out before, the aim of this work is also related to validate the use of batch adsorption experiments for determining the adsorption parameters that can later be used to accurately describe the behavior of a small-scale column test. Thus, batch adsorption experiments were used to determine the paracetamol uptake, adsorption equilibrium as well as the kinetic parameters, which were later employed to calculate the breakthrough profiles for the lab-scale fixed-bed adsorption column. Two models, the first being a numerical solution to the paracetamol molar balance in the fixed-bed and carbon particle, where a heterogeneous diffusion coefficient in the pores related to the amount of adsorbed paracetamol is considered, and the second one being the commonly used constant pattern linear driving force model (CP-LDF), have been compared for the description of the breakthrough profiles. The modeled breakthrough profiles along with the service parameters of rapid small scale column tests were confronted with those experimentally obtained at laboratory, which allowed us to clarify how batch adsorption data should be worked out for achieving a successful description of the behavior of a given adsorbent in fixed-bed adsorption.
2. Materials and methods

2.1. Preparation and characterization of the activated carbon

Olive stones provided by Sociedad Cooperativa Andaluza Olivarera y Frutera San Isidro (Periana, Málaga) were used as the raw material. This abundant and economic residue constitutes an excellent and underutilized carbon precursor. It is not a porous material as supplied, and therefore it has not adsorption capacity by itself; an activation step is necessary to develop any specific surface area. Olive stones were previously ground, washed with distilled water, and dried at 100 °C before their use. The precursor was then impregnated with concentrated commercial H$_3$PO$_4$ (85 % wt, Sigma Aldrich), using a weight ratio of 3/1 (H$_3$PO$_4$/olive stone) at 60 °C for 24 h. This activating agent is known to promote a high mesopore volume development in the resulting activated carbon [24] and [25], which is useful in liquid phase adsorption, as well as a rendering higher carbonization yield than other activation methods thanks to the catalytic aromatization that the biomass undergoes when contacted with phosphoric acid [26], which is beneficial for a better sustainability of the preparation process. The mixture was activated at 500 °C under continuous N$_2$ (99.999%) flow (150 cm$^3$ min$^{-1}$) in a tubular furnace. The activation temperature was reached at a heating rate of 10 °C min$^{-1}$, kept for 2 h and the activated sample was cooled inside the furnace until room temperature. The resulting activated carbon was washed with distilled water at 60 °C to neutral pH and negative phosphate analysis in the eluate. A final heat treatment at 900 °C under inert flow (N$_2$) was carried out, obtaining a thermally treated activated carbon (ACTT). The carbon was weighted to determine the yield of the preparation process (weight % of activated carbon related to weight of raw material, in dry basis, $\eta$=42.4%), ground and sieved to a particle size between 0.3-0.1 mm.
The porous structure was characterized by N\textsubscript{2} adsorption-desorption at -196 °C, and by CO\textsubscript{2} adsorption at 0 °C performed in ASAP 2020 equipment (Micromeritics). The sample was previously outgassed at room temperature for at least 8 hours. From the N\textsubscript{2} isotherm, the apparent surface area (A\textsubscript{BET}) was determined applying the BET equation [27]. The micropore volume (V\textsubscript{t}) and the external surface area (A\textsubscript{t}) were calculated using the t-method [28], [29] and [30] using a non-porous carbon black as standard. The narrow mesopore volume (V\textsubscript{mes}) was determined by the difference between the adsorbed volume of N\textsubscript{2} at a relative pressure of 0.995 and the micropore volume (V\textsubscript{t}). From the CO\textsubscript{2} adsorption data, the narrow micropore volume (V\textsubscript{DR}) and apparent surface area (A\textsubscript{DR}) were calculated using the Dubinin-Radushkevich equation [31]. The size, shape and texture of the ACTT particles were analyzed by scanning electron microscopy (SEM) in a JEOL JSM-840 instrument. Fig. 1 shows a micrograph of the ACTT. From these and similar micrographs, carbon particle size (average range after sieving) was estimated to be 185 ±5 µm. Therefore, a particle radius (R\textsubscript{p}) of 92.5 µm and particle density (ρ\textsubscript{p}) of 1.294 g cm\textsuperscript{-3} measured by water displacement have been used as input parameters for the mass balance equations.

Table 1 summarizes the surface properties of the activated carbon. High values for surfaces area, a balanced meso to microporosity ratio (V\textsubscript{mes}/V\textsubscript{t}) and a high development of wide microporosity (V\textsubscript{t}>V\textsubscript{DR}) are obtained, which constitute valuable features in a diffusion-involved application as the liquid phase adsorption.

The surface chemistry of the sample was analyzed by X-ray photoelectron spectroscopy (5700C model Physical Electronics) with Mg kα radiation (1253.6 eV). The maximum of the C1s peak was set to 284.5 eV and used as reference for shifting the whole
spectrum. As can be seen in Table 1, the carbon used in this work presented surface phosphorus groups. The generation of surface phosphorus groups during \( \text{H}_3\text{PO}_4 \)-activation of biomass have been long proven by our research group, while their striking influence in the surface acidity, kinetic activity and oxidation resistance of the resulting activated carbons have been reported in the past [32] and [33]. A detailed study of XPS P\(_2p\) region revealed that the thermal treatment produced a shift of the spectra to lower binding energies, which means that COPO\(_3\) groups were thermal reduced by the surface of the activated carbon to form lesser oxidized species, such as CPO\(_3\), C\(_2\)PO\(_2\) and C\(_3\)PO, decreasing the surface acidity [34] and [35]. Since some authors [36] have linked the paracetamol adsorption capacity with the acidity and the carbonization temperature in phosphorus-containing activated carbons, it is expected that the heat treatment would produce a lower acidity and polarity of the carbon surface, which will favour the paracetamol adsorption on the resulting ACTT.

**TABLE 1 HERE**

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2.2. Adsorption equipment and procedures

2.2.1. Batch adsorption.

The experimental methods used for the equilibrium and the kinetic studies were the same reported in previous works [37] and [38]. Paracetamol (\( \text{C}_8\text{H}_9\text{NO}_2 \) (99.5%) Sigma-Aldrich, molecular weight: 151.2 g mol\(^{-1}\), melting point: 168-172°C, solubility (20°C): 14 g L\(^{-1}\), pKa: 9.9) solutions were prepared with distilled water at different initial concentrations (1 – 20 mg L\(^{-1}\)). For the equilibrium tests, samples of 100 mL and doses
of 10.0 mg of dry activated carbon were put inside glass flasks and contacted in an
orbital incubator (Gallenkamp, model INR-250) at 200 rpm equivalent stirring rate for
10 days. The adsorbate concentrations were determined by UV spectroscopy ($\lambda_{\text{max}}$: 243
nm) with an UV-Visible (Varian, Model Cary 1E) spectrophotometer. For the kinetic
tests, paracetamol solutions (7 mg L$^{-1}$) were put in contact with activated carbon and
agitated for different times with adsorbent doses of 10.0 mg. The temperatures for the
experiments varied between 15 ºC and 35 ºC.

From the batch tests, the adsorption capacities at equilibrium, $q_e$ (mg g$^{-1}$), were
calculated as:

$$q_e = \frac{C_0 - C_e}{w}$$  \hspace{1cm} (1)

where $C_0$ and $C_e$ represent the initial and the equilibrium concentrations (mg L$^{-1}$) of the
adsorbate in solution, and $w$ is the adsorbent dose (g L$^{-1}$).

The experimental data for paracetamol adsorption at the equilibrium were fit using the
adsorption isotherm model of Langmuir:

$$q_e = \frac{q_L \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$$  \hspace{1cm} (2)

$K_L$ is the equilibrium constant (L mg$^{-1}$), usually related to the enthalpy of adsorption,
and $q_L$ is the equilibrium concentration of the adsorbate (mg g$^{-1}$) on the solid phase
corresponding to a complete coverage (adsorption capacity for a monolayer).

The adsorbed amount of paracetamol, $q_t$, in the kinetic tests was calculated as:

$$q_t = \frac{C_0 - C_t}{w}$$  \hspace{1cm} (3)
where $C_t$ (mg L$^{-1}$) represents the adsorbate concentration in the aqueous phase at time $t$ (min).

The kinetic experimental results have been fitted by a hyperbolic equation previously used by us, [38] and [39], for smoothing the experimental curves, which will be helpful in avoiding noise during subsequent treatment of the experimental data:

\begin{equation}
q_t = \frac{a \cdot q_m \cdot t}{1 + a \cdot t}
\end{equation}

\begin{equation}
\frac{dq_t}{dt} = \frac{a \cdot q_m}{(1 + a \cdot t)^2}
\end{equation}

where $a$ and $q_m$ are empirical parameters related to the kinetic curve shape. $q_m$ represents the asymptotic $q_t$ value in the function at the set experimental conditions. Therefore, $q_t$ tended to $q_m$ at the maximum contact time in the kinetic test.

2.2.2. Column adsorption.

A diagram of the installation used in the adsorption study is showed in Fig. 2. The fixed bed adsorption tests were carried out in a thermostatized glass column (± 0.5 ºC), with internal diameter of 5mm and the length bed varied according to the amount of the activated carbon. A weighted amount of activated carbon was packed between two slices of inert quartz wool inside the column. The ability of the paracetamol to be adsorbed on the quartz fibers was discarded by a previous blank experiment with a quartz wool piece placed as adsorbent inside the column. Paracetamol solution was pumped downflow through the column at controlled flow rate using a peristaltic pump. The breakthrough curves were obtained by continuous monitoring of the effluent concentrations by UV spectrometry.
Before the column test was started, water (6 mL min\(^{-1}\)) was feed to the column for 20 minutes in order to remove the trapped air and to wet the activated carbon porosity. To minimize axial dispersion effects, the bed-length to particle diameter ratio (\(L_b/R_p\)) was larger than 20 for all experiments [40]. Two different sets of experiments were carried out to separate the effects from the concentration, temperature, flow rate and bed length changes. First, four tests were conducted to study the influence of the flow rate (4 and 8 mL min\(^{-1}\)) and the bed length (170 and 230 mg of activated carbon) on the adsorption kinetics at the experimental conditions of the central point of the design (DEO) as proposed in Fig. 3, i.e. 5 mg L\(^{-1}\) and 25 °C.

Second, a DEO experimental design was used for minimizing the number of experiments required to study the influence of the temperature and the concentration, as showed in Fig. 3, while the solution flow and the activated carbon amount were set at 6 mL min\(^{-1}\) and 200 mg, respectively.

### 3. Mathematical models for the mass transfer

#### 3.1. CP-LDF breakthrough process analysis

The linear driving force model (LDF) [41] has been widely applied to model the breakthrough profiles in activated carbons adsorption beds for several pollutants [42], [43] and [44]. It contemplates that the mass transfer rate at a given point of the bed is proportional to the difference between the current concentration of the solute on the adsorbent at a local level and that corresponding when the equilibrium with the bulk
phase is achieved. Under certain conditions, it can be considered that the adsorption fronts follow a constant pattern (CP) behavior, i.e. the front shape is unmodified while it propagates through the adsorption bed. Explicit equations for the breakthrough front can be derived for this CP-LDF [45]. The equation of the CP-LDF model and the Langmuir isotherm was given by LeVan [46] in dimensionless form:

\[
\frac{1}{1 - R_S} \ln \left( \frac{1 - \frac{C}{C_i}}{\left( \frac{C}{C_i} \right)^2} \right) + 1 = N - N \cdot T
\] (6)

where \( N \) is the number of transfer units, and \( T \) and \( R_S \) are the throughput parameter and separation factor respectively, given by:

\[
N = k_i \frac{\rho_b \cdot z \cdot q_i}{u \cdot C_i}
\] (7)

\[
T = \frac{C_i}{q_i} \cdot \frac{1}{\rho_b} \left( u \frac{t}{z} - \epsilon_b \right)
\] (8)

\[
R_S = \frac{1}{1 + K_L \cdot C_i}
\] (9)

in these equations \( C_i \) is the inlet concentration, \( q_i \) is the equilibrium adsorbed amount at \( C_i \) from Langmuir equation, \( u \) is the superficial liquid velocity, \( z \) is the axial position in the bed, \( \epsilon_b \) and \( \rho_b \) are the bed porosity and density, and \( t \) is the time. The intraparticle mass transfer coefficient, \( k_i \), is given by:

\[
k_i = \frac{15 \cdot D_e}{R_p^2} \cdot \frac{\epsilon_b}{1 - \epsilon_b}
\] (10)
where $R_p$ is the radius of the particle and $D_e$ is the effective intraparticle diffusion coefficient, which is experimentally determined using the Reichenberg equation (detailed in 4.2.2. section).

The breakthrough curve equation obtained in working variables is:

$$
 t = t_s - \frac{1}{k_i} \left( 1 + \frac{1}{1 - R_s} \frac{1 - C/C_i}{(C/C_i)^{R_s}} \right)
$$  

(11)

where the stoichiometric time, $t_s$, is written as follows:

$$
 t_s = \frac{W \cdot q_i}{Q \cdot C_i}
$$  

(12)

being $W$ the mass of the carbon and $Q$ the volumetric flow rate.

3.2. Mass balance analysis

3.2.1. Physical assumptions.

The use of two mass transfer resistance models for adsorption is generally accepted as the best choice for describing the adsorption process in activated carbons [47]. A model that considers external-film and diffusion mass-transfers beside axial dispersion along the bed length has been used in this work to calculate the breakthrough profiles under varying operation conditions. The following assumptions are made in the sake of providing an adequate description of the operation of the column:

- Gradients in the concentration profiles of the adsorbate due to radial flow are accepted as negligible. They are excluded by a suitable design of the column ($R_b > 20 R_p$).
- The process operates under isothermal conditions, being ensured by thermostatizing the column using a recirculate water bath.

- The activated carbon particles are treated as spherical and homogeneous in size and density.

- The axial velocity, $v_z$ (m s$^{-1}$), is supposed to be constant and the occurrence of preferential paths is not considered.

- Mass transport between the bulk phase and the solid particle is described by the external-film mass-transfer coefficient, $k_f$ (m s$^{-1}$) [48].

- Intraparticle mass transfer mainly controlled by surface diffusion, represented by an effective diffusion coefficient $D_e$ (m$^2$ s$^{-1}$).

3.2.2. Fluid phase to external surface mass balance.

After assuming the aforementioned hypothesis, a generalized differential equation for the mass balance of the solute which flows through a fixed bed adsorber can be drawn:

$$
\frac{\partial C_b}{\partial t} = -v_z \cdot \frac{\partial C_b}{\partial z} + D_z \cdot \frac{\partial^2 C_b}{\partial z^2} - k_f \cdot \frac{3}{R_p} \cdot \frac{1 - \epsilon_b}{\epsilon_b} \cdot (C_b - C_p)
$$

in this equation $C_b$ is the bulk adsorbate concentration in the water flowing through the bed, $C_p$ is the concentration in the particle external surface, and $D_z$ is the axial dispersion coefficient. The terms of Eq. (13) account the phenomenon for the transient, convective, axial dispersion and external mass transfer across the boundary layer between the bulk and the external surface of the adsorbent, respectively.

The initial conditions and the boundary conditions at the both ends of the bed are:

$t=0; \quad z=0; \quad C_p=0; \quad C_b=0$
\( t=0; \quad z>0; \quad C_p=0 \)

\( t>0; \quad z=0; \quad D_z \cdot \frac{\partial C_b}{\partial z} = v_z/\varepsilon_b \cdot (C_b - C_i) \)

\( t>0; \quad z=L_b; \quad \frac{\partial C_b}{\partial z} = 0 \)

where \( L_b \) is the length of the fixed bed.

The external mass transfer coefficient as well as the axial dispersion coefficient were calculated using the following correlation [49]:

\[
k_f = \frac{D_l \cdot \left(2 + 0.644 \cdot Re^{1/2} \cdot Sc^{1/3}\right) \cdot (1 + 1.5 \cdot (1 - \varepsilon_b))}{2 \cdot R_p} \quad (14)
\]

Being \( Re \) and \( Sc \) the Reynolds and Schmidt numbers, and \( D_l \) the molecular diffusivity for the solute (i.e., paracetamol in water \( 7 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1} \)).

\[
Re = \frac{2 \cdot R_p \cdot v_z \cdot \rho_l}{\mu_l} \quad (15)
\]

\[
Sc = \frac{\mu_l}{D_l \cdot \rho_l} \quad (16)
\]

\[
D_z = D_l = \frac{1.326 \cdot 10^{-4}}{\mu_l^{1.14} \cdot V_b^{0.589}} \quad (17)
\]

where \( \rho_l \) (1000 kg m\(^{-3}\)) and \( \mu_l \) (0.00089 kg m\(^{-1}\) s\(^{-1}\)) are the density and viscosity of the fluid through the column (for Eq (17) \( \mu_l = 0.89 \text{ cP} \)), and \( V_b \) (191 cm\(^3\) mol\(^{-1}\)) is the molar volume of the solute at its normal boiling point. \( V_b \) has been calculated using the estimation formula proposed by Treybal [50].

3.2.3. Mass balance within the particles.
Since diffusion is considered to be predominant in the mass transfer through the micropore system of the activated carbon [47] and [51], the mass balance within a differential radial section of an adsorbent particle can be described by the following equation:

\[ \varepsilon_p \frac{\partial q_r}{\partial t} = - \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 N_s \right) \]  

(18)

where \( \varepsilon_p \) is the particle porosity, \( q_r \) the adsorbed concentration at the radial r position in the spherical particle.

The diffusion molar flux \( N_s \) can be expressed according to the Fick’s law:

\[ N_s = - \left( D_e \frac{\partial q_r}{\partial r} \right) \]  

(19)

As for the estimation of the effective diffusion coefficient, \( D_e \), it has been detailed in the 4.2.2. section. Finally, the required initial and boundary conditions are:

\( t=0; \quad q_r = 0 \)

\( t>0; \quad r=0; \quad \frac{\partial q_r}{\partial r} = 0 \)

\( t>0; \quad r=R_p; \quad N_s = k_f \left( C_b - C_p \right) \)

In the approach proposed in this work, the surface concentrations profiles along the radius of the particle are averaged by means of the assumption of parabolic concentration profiles of the solute within the pores. This approximation has been found to be trustworthy when comparing these profiles with those obtained from the rigorous approach [52]. As a consequence of the parabolic concentration profile approximation, the mass balance equation can be simplified as follows:
\[
N_s = 5 \cdot \frac{D_e}{R_p} \cdot (q_{cp} - \bar{q})
\]  

(20)

\[
\frac{\partial \bar{q}}{\partial t} = -15 \cdot \frac{D_e}{R_p^2} \cdot (q_{cp} - \bar{q})
\]  

(21)

where \(\bar{q}\) represents the mean concentration of solute adsorbed in the adsorbent particle and \(q_{cp}\) stands for the adsorbed concentration at the solid external surface which is in equilibrium with \(C_p\). Last, the boundary condition at the external surface of the particle requires that the diffusion flow entering must be equal to the molar transfer rate through the liquid film around the particle:

\[
N_s = 5 \cdot \frac{D_e}{R_p} \cdot (q_{cp} - \bar{q}) = k_f \cdot (C_b - C_p)
\]  

(22)

This equation allows to establishing the \(C_p\) value. This is possible because the adsorbed concentration \(q_{cp}\) may be related to the fluid phase concentration \(C_p\) in that same location, at \(r=R_p\), by an adequate adsorption equilibrium isotherm.

4. Results and discussion

4.1. Adsorption equilibrium

The equilibrium adsorption isotherms of paracetamol solutions at 15, 25 and 35 °C are showed in Fig. 4. The isotherms resulted as type L of Giles classification [53] and the observed uptakes for low equilibrium PA concentration are close to the values reported for P-containing activated carbons prepared at 800º C [36] or activated carbons prepared by physical activation with CO\(_2\) [22]. However, it is important to note that the paracetamol adsorption have been studied in the present work using one order of magnitude lower than that used in the reported works. At higher paracetamol
concentrations, lateral interaction between adsorbed species and/or multilayer adsorption may enhance the adsorbed amount by the activated carbon [20].

In our case, the increase on adsorption temperature produces a decrease in the paracetamol adsorbed amount, which suggests the exothermic nature of the adsorption process. The Langmuir adsorption parameters were calculated using a non-linear regression fitting procedure. The values of $K_L$, $q_L$ and $r^2$ (determination coefficient) are showed in Table 2.

FIGURE 4 HERE

The free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$) changes were calculated by the following equations: the free energy change related to the equilibrium constant (Eq. 23), the Van’t Hoff’s (Eq. 24) for the enthalpy change, and the Gibbs-Helmholtz’s (Eq. 25) to estimate the entropy change. The values obtained are showed in Table 2.

$$\Delta G = -RT \ln K_L$$  \hspace{1cm} (23)

$$\frac{\partial \ln K_L}{\partial T} = \frac{\Delta H}{R \cdot T^2} \Rightarrow \ln K_L = \ln K_{L0} - \frac{\Delta H}{R \cdot T}$$  \hspace{1cm} (24)

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$  \hspace{1cm} (25)

in these equations, $R$ is the gas constant (8.31 J mol$^{-1}$ K$^{-1}$), $T$ is the absolute temperature (K), and $K_{L0}$ is the pre-exponential factor, i.e., the value of $K_L$ when $T$ tends to infinite.
The negative values of $\Delta G$ from Eq. (23) indicate the spontaneity of the adsorption process. The average molar values of $\Delta G$ are quite influenced by the temperature.

The low negative value of the enthalpy from the slope in the linear regression of Eq. (24) confirms the exothermic nature of the adsorption process. However, there are some studies that report the paracetamol adsorption process on activated carbons being endothermic [20] and [22]. These discrepancies are accountable to the higher paracetamol concentration used in those studies ($>100$ mg L$^{-1}$), enabling the formation of dimers and micelles. When these agglomerations appear, the adsorption is favored as the temperature increases due to a lower amount of dimers in solution and an increased diffusion of the solution through the porosity of the activated carbon. This is not the case of the study showed in this paper, where the low concentrations do not favor the formation of dimers and micelles.

Positive values of the adsorption entropy changes from Eq. (25) are coherent with a decrease of the freedom of the molecules in the fluid phase when they are adsorbed.

### 4.2. Kinetic study

#### 4.2.1. Empirical model for the liquid phase adsorption.

The kinetic results obtained at three temperatures are showed in Fig. 5. It is clear that the adsorption rate and yield increase with increasing the temperature. This is due to the enhancement of diffusion rate of the solute through the porous structure. It can be observed (plot inset in Fig. 5a) that $q_t$-$t$ curves for different temperatures intersect at long times, and the higher adsorption temperature is, the lower time to reach the equilibrium state is and the lower amount of paracetamol adsorbed in equilibrium is.
Table 3 compiles the fitting coefficients, whereas Fig. 5b presents the PA adsorption rate at different temperatures derived from Eq. (5). A sharp decrease in the adsorption rate is observed for the first minutes of contact time. This step corresponds to the surface coverage in the most available adsorption sites, probably on the more accessible and wider pores. A second adsorption stage runs for 3 h approximately with an intermediate decreasing rate. The last phase leads to the equilibrium concentrations, and could take extremely long times of contact time, in the range of several days.

**FIGURE 5 HERE**

### 4.2.2. Effective diffusion coefficients.

The effective diffusion coefficient \(D_e\) can be obtained from the data of PA adsorption rate obtained in the batch study according to the procedure given by Reichenberg [54]:

\[
F(t) = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{n^2 \pi^2 R_p^2}{D_e R_g^2} D_e t \right) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -n^2 B t \right) \tag{26}
\]

where \(B\) is the time constant,

\[
B = D_e \frac{\pi^2}{R_p^2} \tag{27}
\]

and \(F(t)\) is the fractional uptake \((q_t/q_e)\) at time \(t\). By applying the Fourier transform and integration, Reichenberg obtained the following approximation for \(F(t) < 0.85\):

\[
B \cdot t = \left( \sqrt{\pi} - \sqrt{\pi - \left( \pi^2 \cdot F(t)/3 \right)} \right)^2 \tag{28}
\]

The values of the second member in Eq. (28), i.e. each observed value of \(F(t)\), may be plotted vs \(t\) to distinguish between adsorption controlled by external or internal
diffusion. If it is linear and passes through the origin, then the adsorption rate is
controlled by the diffusion within the particles. Otherwise, the adsorption may be also
governed by the film diffusion considered as a external mass transfer. The results are
summarized in Table 3. The $B\cdot t$ plots for each adsorption temperature are shown in Fig.
The linearity of the plots ($r^2 > 0.976$) and the almost zero value of Y-intercept
indicate that the mass-transfer process is controlled by the internal diffusion. From the
slope of the slope of the $B\cdot t$ plot, effective diffusion coefficients have been obtained at
15, 25 and 35º C. They have been termed heretofore as homogeneous diffusion
coefficients, in clear contrast to those obtained considering that the diffusion coefficient
varies with the surface coverage of PA, which are referred as heterogeneous diffusion
coefficients. The relationship between heterogeneous $D_e$ and surface coverage has
been reflected by using the Vermeulen equation [55]:

\begin{equation}
\frac{q_t}{q_e} = \left[1 - \exp\left(-\frac{D_e \pi^2 t}{R_p^2}\right)^{0.5}\right]^{-1}
\end{equation}

\begin{equation}
D_e = \frac{-R_p^2}{\pi^2 t} \ln\left[1 - \left(\frac{q_t}{q_e}\right)^2\right]
\end{equation}

The hyperbolic Eq (4) has been used for the estimation of $q_t$. Eq (4) and (30) have been
employed for establishing the relationship between the diffusion coefficient and the
surface coverage, i.e. the adsorbed amount of paracetamol. First, $D_e$ for each $t$ is
estimated from (30), then, the obtained data were fitted to an exponential empirical
equation:
\[ D_e = b \cdot \exp \left( \frac{c}{t + d} \right) \]  

(31)

\[ b, c, \text{ and } d \text{ are empirical parameters. The hyperbolic Eq (4) can be combined with (31) in order to obtain an expression which relates the diffusion coefficient with } q_t: \]

\[ D_e = b \cdot \exp \left( \frac{c}{(q_e - q_t) + d} \right) \]  

(32)

The fitting of \( D_e \) vs \( q_t \) was conducted using contact times higher than 200 min to avoid the underestimation of \( D_e \) at low contact times, where the wetting process of the initially dry micropores hinders the mass transfer of the adsorbate through the particle. Table 3 compiles the resulting fitting coefficients.

**FIGURE 7 HERE**

Fig. 7 presents the relationship between the effective diffusion coefficient and the adsorbed amount of paracetamol (i.e. PA surface coverage) for a given initial concentration (7 mg L\(^{-1}\)) and different temperatures. As expected the calculated curves corroborate that an increase in the temperature of the batch adsorption experiment are answered by an overall increase in the value of the diffusion coefficients. As for the dependence of diffusion with the adsorbed amount of PA, \( D_e \) values decrease with the surface coverage (or time) due to the depletion of the available free adsorption sites that are necessary to allocate the adsorbed PA molecules that are diffusing over the surface.

This decrease of the diffusion coefficient can also be explained in terms of the wide pore structure distribution of the pore network and the heterogeneity of the surface chemistry of the activated carbon, which will render not only different energies of interaction between the adsorbate and the adsorbent depending on the surface coverage of PA over the carbon surface, but also a different mobility of the adsorbed PA
molecule on the pore network. Thus, as the adsorption phenomenon proceeds (long
times), paracetamol will be adsorbed first in the more energetically favorable and
accessible adsorption sites at a fast rate. When the most favored sites are fully covered
by PA, the mass transport becomes progressively controlled by a slower diffusion of the
paracetamol into the less energetically favorable and isolated adsorption sites.

**TABLE 3 HERE**

### 4.3. Column adsorption studies

Fig. 8 presents a scheme of a breakthrough curve for paracetamol adsorption on ACTT,
where the procedure followed for the calculation of the breakthrough curve by solving
the mass balance to the fixed-bed adsorber is also detailed. The mathematical calculus
was carried out applying the finite differences method with 75 points to the length
variable (z) in Eq. (13) of the mass balance for the fixed-bed adsorber. For each i point,
first $C_{pi}$ is determined from Eq (22), then $\partial \tilde{q}_i/\partial t$ is estimated from Eq (21) using $C_{pi}$,
the Langmuir constants and the heterogeneous diffusion coefficient determined from
batch adsorption experiments and Eq (2) and (32). Third, since Eq (13) have been
discretized in the $z$ variable following the finite differences method [56], $\partial C_{bi}/\partial t$ can
be calculated by evaluation of the convective and dispersive flows from the $i$-$l$ point
and dispersive flow from the $i+l$ point, the convective flow from $i$ to the $i+l$ point, and
the flow through the stationary liquid film over the carbon particle, which is estimated
using the freshly determined value of $C_{pi}$. The proper boundary conditions are
considered in the case of 1$^{\text{st}}$ and 75$^{\text{th}}$ point. Finally, a 4$^{\text{th}}$ order Runge-Kutta method is
used for solving in time $\partial \tilde{q}_i/\partial t$ and $\partial C_{bi}/\partial t$ for the 75 points. The $C_{b}$ value at the 75$^{\text{th}}$
point, the one localized at the end of the fixed bed, is stored and used for obtaining the
breakthrough profile.

It is important to note that the kinetic and equilibrium adsorption parameters obtained in
batch system, i.e. adsorption isotherm constants and the effective diffusion coefficient,
have been used for solving the mass balance equations that allow the prediction of the
breakthrough profile. Note that the solution of these equations allows the determination
of the time for the breakthrough appearance or bed service time (BST), which is
established as the time at what the outlet concentration reach the $C/C_i = 0.05$ value, and
the shape of the breakthrough profile, which is related to the height of the mass transfer
zone ($H_{MTZ}$). These are actually critical parameters for determining the operation and
the dynamic response of an activated carbon when used as adsorbent for an adsorption
bed that cannot be directly determined from batch adsorption experiments. In simple
terms, the breakthrough time is proportional to the capacity of the adsorbent, while
inversely related to the $H_{MTZ}$ value. For a given inlet concentration, the adsorption
capacity of the adsorbent can be determined if its adsorption isotherm is established.
Contrariwise, the height of mass transfer zone does not keep a direct relationship to any
specific kinetic parameter, and it results from the interaction between the
hydrodynamics of the experimental set-up and the surface properties (surface chemistry,
pore structure) of the adsorbent [57]. Since breakthrough time and therefore bed service
time are dependent on both $H_{MTZ}$ and adsorption capacity, and there is no direct
relationship between $H_{MTZ}$ and the kinetic and thermodynamic batch adsorption
parameters, the numerical solving of the mass balance equations detailed here is
proposed for predicting them.

**FIGURE 8** HERE
The validity of some of the assumptions made in section 3.2.1 have been checked by analyzing the dimensionless numbers that dictate the dominating processes during the operation of the fixed bed adsorber. Table 4 compiles the experimental values of the adsorbent and the bed that have been used for this purpose, along with the values of the mentioned dimensionless numbers concerned. The Reynolds values (Re) between 0.97 and 1.96 indicate that a laminar flow regime is governing in the fixed bed, and that liquid flow through the column is meanly produced by convection, hence the Schmidt number (Sc) was higher than 12.71 for all the column experiments. The high values of Peclet number (Pe), between 1931 and 3778, as well as the low axial dispersion coefficient ($7 \cdot 10^{-10} \text{m}^2 \text{s}^{-1}$, estimated from equation (17)) suggest that the influence of this phenomenon on the column behavior is negligible. Values of the Biot number (Bi) and the mass transfer coefficient ($k_i$) are also high, pointing out the absence of limited mass transfer through the stationary layer of liquid around the particles of the adsorbent.

Fig. 9 to 12 show the breakthrough profiles obtained for the paracetamol adsorption in the activated carbon fixed-bed under different operating conditions. All the experimental breakthrough curves follow the typical S-shaped curve for column operation with favorable adsorption isotherms [58]. In all the curves, the experimental data are identified by symbols, whereas the breakthrough curves calculated by CP-LDF are plotted using discontinuous line and those obtained from the solution of the numerical model with heterogeneous diffusion coefficient proposed in this work have been represented by continuous lines. The profiles are reported in terms of treated
volume for easing the comparison among results obtained using different experimental conditions (flow rate, inlet concentration, temperature…). It can be observed in Fig. 9-12 how the thermodynamic and kinetic parameters obtained in stirred tank and then introduced in the numerical solution proposed in this work for the mass balance to the fixed-bed adsorber can satisfactorily explain the experimental curves when the heterogeneous effective diffusion coefficient approach is considered. In contrast, CP-LDF could not provide an accurate description of the breakthrough profile. The reasons will be discussed in detail above.

4.3.1. Effect of the flow rate.

The experiments displayed in Fig. 9 were conducted at variable flow rates to establish the possible influence of mass transfer in the film of stationary liquid that surrounds the particle. The rest of the experimental conditions were those used for the central point, i.e. 25 °C, 5 mg L\(^{-1}\) of paracetamol at the column inlet and 200 mg of activated carbon. It was found that the variation of the flow rate has a negligible impact on the shape of the breakthrough curves, confirming the absence of external mass transfer control, as predicted from the Biot numbers in Table 4. This finding was further corroborated by simply solving the mass balance to the fixed bed and the carbon particle proposed in 3.2.2. and 3.2.3. sections while removing the consideration of external mass transfer (thus, \(C_p = C_b\)). The obtained profile was identical to that obtained when the mass balance was solved upon consideration of external mass transfer in the liquid film.

FIGURE 9 HERE
4.3.2. Effect of the amount of activated carbon.

The effect of axial dispersion was analyzed by carrying out experiments at 25 °C, PA concentration of 5 mg L⁻¹, flow rate of 6 mL min⁻¹ and different bed lengths (2.6-3.2 cm). As observed in Fig. 10, the breakthrough time is affected by the amount of activated carbon. The behavior of the breakthrough profile at different lengths, which shows a similar shape no matter the chosen bed length, leads to the conclusion that it does not exist any back mixing or axial dispersion problem in the column. This assert is in accordance with that drawn from the high values of the Peclet number showed in Table 4, and was again confirmed by the absence of any relevant difference when the mass balance in 3.2.2 was solved without including the axial dispersion term. Therefore, and under the operating conditions selected for this work, the mass balance to the small column can be solved without considering axial dispersion and external mass transfer control, and consequently the numerical solution can be simplified reflecting these conclusions. Note that, under such conditions, the CP-LDF can theoretically be used for describing the behavior of the fixed-bed adsorber [41]. Nevertheless, by following the approach proposed in this work the breakthrough profiles have been modeled obtaining a much higher accuracy in the description of the experimental curves, as can be seen along Fig. 9 to 12.

FIGURE 10 HERE
4.3.3. Effect of adsorption temperature and PA concentration.

Fig. 11a shows the breakthrough curves for the PA adsorption at different temperatures, in all cases the inlet concentration was kept at 5 mg L$^{-1}$, the flow rate at 6 mL min$^{-1}$ and a bed of 200 mg of activated carbon was used. It can be seen that the breakthrough time ($C/C_i \approx 0.05$) decreased when temperature increases, while the saturation times ($C/C_i \approx 0.95$) were higher for those runs performed at lower temperature, and the height of the mass transfer zone decreased a 20% when raising the temperature from 15 to 35º C. These modifications are reflecting the higher values for the diffusion coefficients and the lower paracetamol adsorption capacities at higher temperatures that were already found in the batch study.

The effect of the inlet concentration of paracetamol on the breakthrough profiles has also been analyzed and featured in Fig. 11b. Again, the expected behavior is found when concentration decreases, finding a great increase the breakthrough time, a lower adsorption capacity and similar value of $H_{MTZ}$. For all the experimental conditions tested in this work, the worse profile simulation was found for the experiment conducted at $C_i = 3$ mg L$^{-1}$. The main reason of the inaccurate prediction of the breakthrough time seems to be the increase of the uncertainty in the determination of the adsorption capacity of the ACTT at low concentrations of PA from the batch study.

Finally, in order to be useful an adsorption model for fixed-bed adsorbers should be able to truthfully predict the breakthrough behavior at different conditions than those used for the estimation of the adsorption parameters. In this sense, Fig. 12 shows the breakthrough curves at 18 and 32 ºC, respectively, using 6 mL min$^{-1}$, 200 mg of activated carbon and 4 and 6 mg L$^{-1}$ of paracetamol. Since the thermodynamic and
kinetic studies were carried out at 15, 25 and 35 °C, the thermodynamic and kinetic adsorption parameters values fed to the models were estimated using a linear interpolation method. A good concordance was found with the mathematical solution of the mass balance and the \( q_t \)-dependent \( D_e \), while CP-LDF failed to reproduce the bed behavior. It has been found once more that the curves for the higher concentration at the inlet are better described than those obtained using low concentration of paracetamol, highlighting the reliance of the accuracy of the proposed model in a precise determination of the adsorption isotherm during the batch study.

**FIGURE 12 HERE**

4.3.4. Design parameters and models comparison.

Table 5 presents the experimental values of adsorbed paracetamol amount (\( q_{exp} \)) as well as the BST and H\(_{MTZ} \) obtained for all the tested operational conditions. It can be seen that the adsorbed amounts ranged between 68 and 89 mg of PA per gram of activated carbon, while the low values of the H\(_{MTZ} \) results in an actual use of 60 to 80% of the available paracetamol remediation capacity before the PA outlet concentration reached the selected limit. As for the calculus of the design parameters, there are only few samples in the literature about using the adsorption parameters obtained from the batch studies in order to estimate the fixed bed behavior [51 o 59] of an adsorbent. In this study, the CP-LDF and the numerical solution of the mass balances have been employed for that purpose, and the resulting breakthrough profiles for each model have been shown along with the experimental data in Figs 9 - 12. Table 5 compiles the estimated design parameters for every tested operation conditions. It can be seen that the paracetamol adsorptivities calculated using the mass balance procedure are very close to
those obtained from the experimental breakthrough profiles. Similarly, $H_{MTZ}$ and BST are accurately predicted for all the tested experimental conditions. Furthermore, the high values of $r^2$ indicate that the proposed model can reproduce fairly well not only BST and $H_{MTZ}$, but also most of the experimental breakthrough profile. Inversely, the CP-LDF model cannot be used for a satisfactory determination of the operation behavior of the fixed bed adsorbed. The lack of accuracy undeniably relies on the approach adopted for estimating the diffusivity, since CP-LDF cannot reflect the dependence of the diffusivity coefficient with adsorbed amount that is known to be not necessarily constant in rapid small-scale column tests [18], especially in the case of the highly heterogeneous pore structure of activated carbons.

**TABLE 5 HERE**

### 5. Conclusions

Activated carbon has been prepared by chemical activation of olive stones with phosphoric acid, obtaining a porous carbon material with a well-developed porous structure and specific surfaces area close to 1000 m$^2$ g$^{-1}$. Adsorption of paracetamol (a model emerging pollutant) at low concentration (0.3 to 10 mg L$^{-1}$) and mild temperatures (from 15 to 35º C) has been studied using discontinuous (batch) and flow column adsorption experiments. The adsorption isotherm is well described using the Langmuir model, showing adsorption capacities of ca. 100 mg g$^{-1}$ at 9 mg L$^{-1}$, a value that is only slightly influenced by temperature. Kinetic studies in discontinuous batch experiments have been used for the estimation of effective homogeneous and heterogeneous diffusion coefficients. In the latter case, an empirical equation has been drawn to relate the heterogeneous diffusion coefficient with the surface coverage of paracetamol. The effectiveness of the H$_3$PO$_4$-activated carbon for paracetamol removal has also been studied using rapid small-scale column experiments. The activated carbon
showed high bed service times and reduced heights of the mass transfer zone due to the favorable adsorption of paracetamol on its surface. The effects of operational variables (temperature, flow rates, fixed-bed length and inlet concentration) have been analyzed using a design of experiments. The most important finding in this work was the possibility of accurately modeling the breakthrough behavior of the fixed-bed adsorber by using the kinetic and thermodynamic parameters obtained from the batch experiments. Inappropriate handling of the data obtained from the batch experiments and the use of simplified models that considers a constant diffusion coefficient like CP-LDF do not allow a trustworthy prediction of the design parameters of the column, like BST or H_{MTZ}. In contrast, by using the adequate experimental and boundary conditions, mathematical tools, model considerations and a diffusion coefficient related to the surface coverage of the pollutant, it is possible to attain from simple batch experiments a precise knowledge of the performance of a given adsorbent in column adsorption, which allows an accurate prediction of the breakthrough profile, BST and H_{MTZ}. 

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**References**


Table 1. Physico-chemical properties of ACTT.

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Table 2. Parameters obtained from equilibrium / thermodynamics study

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Table 3. Parameters obtained from the kinetic study

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Table 4. Operation variables for the adsorption column process.

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Table 5. Experimental and design parameters for breakthrough curves.

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*adsorption capacities ($q_{cal}, q_{exp}$) have been calculated to relative concentration of $C/C_i = 0.95$