Chemical Engineering Journal 279 (2015) 18–30

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Removal of paracetamol on biomass-derived activated carbon: Modeling the fixed bed breakthrough curves using batch adsorption experiments

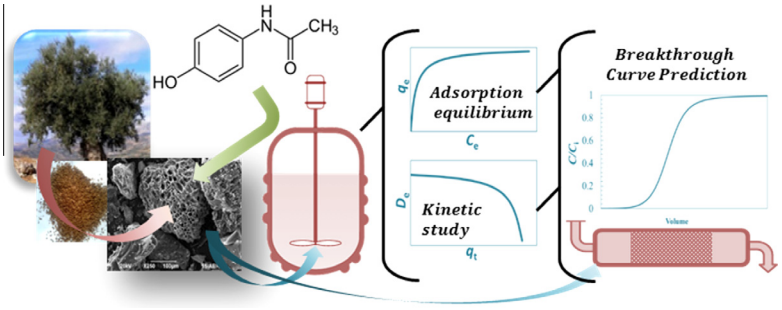
F.J. García-Mateos, R. Ruiz-Rosas, M.D. Marqués, L.M. Cotoruelo, J. Rodríguez-Mirasol *, T. Cordero

Universidad de Málaga, Andalucía Tech, Departamento de Ingeniería Química, Escuela Técnica Superior de Ingeniería Industrial, Campus de Teatinos s/n, 29071 Málaga, Spain

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.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 March 2015
Received in revised form 27 April 2015
Accepted 27 April 2015
Available online 5 May 2015

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

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.

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 [1–3]. Since these compounds have biological activity, there exist scientific and social concerns to control the impact of these

* Corresponding author. Tel.: +34 951 952 385.
E-mail address: mirasol@uma.es (J. Rodríguez-Mirasol).

http://dx.doi.org/10.1016/j.cej.2015.04.144
1385-8947/

Nomenclature

a	empirical parameter (s^{-1})
A_{BET}	specific surface area by Brunauer, Emett, Teller method ($m^2\ g^{-1}$)
A_{DR}	Dubinin Radushkevich surface area ($m^2\ g^{-1}$)
A_t	external area ($m^2\ g^{-1}$)
B	time constant (s^{-1})
b	empirical parameter ($m^2\ s^{-1}$)
c	empirical parameter (s)
C	outlet concentration ($mg\ L^{-1}$)
C_0	initial concentration ($mg\ L^{-1}$)
C_b	paracetamol bed concentration ($mol\ m^{-3}$)
C_e	equilibrium concentration ($mg\ L^{-1}$)
C_i	inlet concentration ($mg\ L^{-1}$)
C_p	concentration in the particle external surface ($mol\ m^{-3}$)
C_t	concentration at time t ($mg\ L^{-1}$)
d	empirical parameter (s)
D_e	effective internal diffusion coefficient ($m^2\ s^{-1}$)
D_l	molecular diffusivity of the solute in water ($m^2\ s^{-1}$)
D_s	surface diffusion coefficient ($m^2\ s^{-1}$)
D_z	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 ($mL\ min^{-1}$)
$\bar{q}$	mean concentration of solute adsorbed in the adsorbent particle
q_{cal}	calculated adsorption capacity from models at $C/C_i = 0.95$ ($mg\ g^{-1}$)
$q\|_{Cp}$	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

ε_b	bed porosity
μ_l	fluid dynamic viscosity (cP)
η	yield
ρ_b	bed density ($kg\ m^{-3}$)
ρ_l	fluid density ($kg\ m^{-3}$)
ρ_p	particle density ($kg\ m^{-3}$)

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 [1,4–6]. 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, [7,8], 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 [9,10]. 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 [11–13]. 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 [14,15]. 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 [17–19]. Even so, most of the laboratories are equipped for the determination of the