Contents lists available at ScienceDirect

Chemical Engineering Research and Design

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

Modeling adsorption rate of tetracyclines on activated carbons from aqueous phase

R. Ocampo-Pérez[a,*], R. Leyva-Ramos[a], J. Rivera-Utrilla[b], J.V. Flores-Cano[b], M. Sánchez-Polo[b]

[a] Centro de Investigación y Estudios de Posgrado, Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Av. Dr. M. Nava No. 6, San Luis Potosi 78210, SLP, Mexico

[b] Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

ARTICLE INFO

Article history:
Received 14 February 2015
Received in revised form 23 June 2015
Accepted 16 September 2015
Available online 26 September 2015

Keywords:
Activated carbon
Adsorption rate
Diffusional models
Surface diffusion
Tetracyclines

ABSTRACT

The adsorption rate of three tetracyclines (TCs) (tetracycline, oxytetracycline, chlortetracycline) on two activated carbons (ACs) were investigated in this work. The experimental adsorption equilibrium data of the TCs on both carbons was obtained in a batch adsorber at T = 298 K and pH range of 4–5, and the Langmuir isotherm better interpreted the experimental data than the Freundlich isotherm. The adsorption of TCs on the ACs was mainly due to π–π interactions. The rate of adsorption of TCs was interpreted using kinetic models along with diffusional models. The pseudo-first-order and pseudo-second-order were fitted to the experimental concentration decay curves of the TCs for the adsorption of TCs on ACs. The first-order kinetic model matched reasonably well the experimental concentration decay data, but the rate constant, k_1, considerably decreased with time. Thus, the rate of adsorption of TCs on ACs cannot be interpreted by the first-order kinetic model. The pore volume diffusion model (PVDM) and the pore volume and surface diffusion model (PVSDM) were also applied to interpret the rate of adsorption of TCs. The PVDM overpredicted the experimental concentration decay data indicating that intraparticle diffusion was due to both pore volume and surface diffusion mechanisms. The PVSDM fitted quite well the experimental concentration decay data of the TCs on both ACs, showing that the intraparticle diffusion of TCs is due to the pore volume diffusion, as well as the surface diffusion. Furthermore, the contribution of surface diffusion is directly dependent on the adsorption capacity of the carbons because the concentration of TCs adsorbed on the surface is the driving force of surface diffusion. Additionally, the contribution of surface diffusion is affected by the time and radial position.

1. Introduction

Tetracyclines (TCs) are extensively used for human therapy and the livestock industry for their antimicrobial activity against a wide variety of bacteria (Mathers et al., 2011; Gao et al., 2012a). Due to their low cost, TCs are also used as a food additive to enhance the growth rate of animals. TCs are released into the environment by water discharges from the manufacture and formulation of drugs, animal farms and disposal of unused or expired pharmaceutical products. Most of the TCs (50–80%) administered to livestock are excreted through the feces and urine as unmodified parent compounds. As a result, TC residues are commonly found in wastewater treatment plants (Lin et al., 2009).

TCs have been detected at concentrations ranging from 0.11 to 4.20 μg/L in surface waters, while concentrations in

* *Corresponding author.* Tel.: +52 4448132157.
E-mail address: raul.ocampo@uaslp.mx (R. Ocampo-Pérez).
http://dx.doi.org/10.1016/j.cherd.2015.09.011

Nomenclature

B	constant of the Langmuir isotherm related to the heat of adsorption (L/mg)
C_A	concentration of tetracycline in aqueous solution (mg/L)
C_{A0}	initial concentration of tetracycline in solution (mg/L)
C_{Ae}	final concentration of tetracycline at equilibrium in solution (mg/L)
$C_{A,r}$	concentration of tetracycline in the pore volume at a distance r (mg/L)
$C_A\|_{r=R_p}$	concentration of tetracycline in the solution at the external surface of GAC ($r = R_p$) (mg/L)
d_p	average particle diameter of GAC (cm)
D_{AB}	molecular diffusion coefficient at infinite dilution (cm^2/s)
D_{ep}	effective pore volume diffusion coefficient (cm^2/s)
D_s	effective surface diffusion coefficient (cm^2/s)
k_1	rate constant for the first-order reaction (h^{-1})
k_2	rate constant of the second-order kinetic model (g/(mg h))
K_f	parameter of Freundlich isotherm ($mg^{1-1/n}\,L^{1/n}/g$)
k_L	external mass transfer coefficient (cm/s)
m	mass of GAC (g)
N	number of experimental data
n	parameter of the Freundlich isotherm
q_e	mass of tetracycline adsorbed at equilibrium per mass of GAC (mg/g)
$q_{e,exp}$	experimental mass of tetracycline adsorbed per mass of GAC (mg/g)
$q_{e,pred}$	mass of tetracycline adsorbed per mass of GAC predicted with the isotherm model (mg/g)
q	mass of tetracycline adsorbed per mass of GAC at time t (mg/g)
r	distance in radial direction of GAC (cm)
R_p	radius of the particle (cm)
S	external area of the solid particles per adsorbent mass (cm^2/g)
t	time (s or min)
T	temperature (K)
V	volume of the tetracycline solution (mL or L)
V_P	pore volume per unit mass of GAC (cm^3/g)
X_m	maximum mass of tetracycline adsorbed onto GAC (mg/g)

Greek letters

ε_p	void fraction of GAC
ϕ_A	dimensionless concentration of tetracycline in the solution
ϕ_{exp}	experimental dimensionless concentration of tetracycline in the solution
ϕ_{pred}	dimensionless concentration of tetracycline in solution predicted with the model
ρ_p	particle density of GAC (g/cm^3)

effluents from wastewater treatment plants ranged from 46 to 1300 ng/L for tetracycline, 270 to 970 ng/L for chlortetracycline, and 240 ng/L for oxytetracycline (Gao et al., 2012a; Lin et al., 2009; Yang et al., 2005; Ternes et al., 2002; Stackelberg et al., 2007). Batt et al. (2007) and Ternes et al. (2002) found that biodegradation and chlorination processes only slightly degrade TCs, explaining their presence in the effluents from treatment plants. It is important to point out that traces of these antibiotics in the environment can make microorganisms more resistant to these antibiotics, and humans may be exposed to antibiotics *via* drinking water.

The US Environmental Protection Agency recommended the adsorption on activated carbon as the best available technology for removing non-biodegradable toxic organic compounds from drinking water and industrial wastewater (USEPA, 1991). The TCs can be removed from aqueous solutions by adsorption on different adsorbents such as $MnFe_2O_4$/activated carbon composites (Shao et al., 2012), clays (Chang et al., 2012), graphene oxide (Gao et al., 2012b), multiwalled carbon nanotubes (Zhang et al., 2011) and sludge-derived adsorbents (Rivera-Utrilla et al., 2013).

The adsorption mechanism of TCs on carbonaceous materials is mainly governed by dispersive interactions between the π-electrons in the graphene layers of the carbon materials and the π-electrons in the aromatic rings of TCs (Rivera-Utrilla et al., 2013). This type of interaction can be also affected by the electrostatic adsorbent–adsorbate interactions when the adsorption is occurring at pH values causing TC protonation (Rivera-Utrilla et al., 2013). In a previous study, the high adsorption capacity of sludge-derived adsorbents toward TC was attributed to an elevated content of metallic species and the affinity of TCs to form complexes with the metals on the surface of these materials (Rivera-Utrilla et al., 2013). It was also found that the presence of bacteria reduced the adsorption/bioadsorption of TCs on activated carbon by weakening the interactions between the adsorbate and the biofilm formed on the carbon surface.

The overall adsorption rate of TCs on sludge-derived adsorbents was interpreted using kinetic models (first-order, second-order and Langmuir) and diffusional models (pore volume diffusion and surface diffusion) (Ocampo-Pérez et al., 2012a). The first-order kinetic model provided the best interpretation of TC adsorption rate on all adsorbents, and the rate constant was linearly dependent upon the macropores and mesopores volume of the adsorbents. Additionally, the intraparticle diffusion controlled the TC adsorption rate and the contribution of pore volume diffusion to the total intraparticle diffusion represented more than 80%. Hence, surface diffusion did not play a significant role in the intraparticle diffusion of TC in the sludge-derived adsorbents.

The design of an adsorption column requires information on both the adsorption rate and the adsorption capacity of the adsorbent (adsorption isotherm). The adsorption rate in porous solids can be predicted by kinetic and diffusional models. In the latter models, the overall adsorption rate is controlled by pore volume diffusion, surface diffusion or both (Leyva-Ramos et al., 2009). The dependence of the porous structure on the adsorption rate has been also incorporated in some diffusional models (Borrelli et al., 1996; Yang and Al-Duri, 2001).

The adsorption mechanism of TCs on different adsorbents has been extensively studied, but no work has been reported on the diffusion mechanism controlling the intraparticle diffusion of TCs in activated carbons.

The main objective of this work was to interpret the overall adsorption rate of three TCs (tetracycline, oxytetracycline and chlortetracycline) on commercial activated carbons by using diffusional and kinetic models. Besides, the overall rate of