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Research article

Overall adsorption rate of metronidazole, dimetridazole and diatrizoate on activated carbons prepared from coffee residues and almond shells

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ABSTRACT

This study analyzed the overall adsorption rate of metronidazole, dimetridazole, and diatrizoate on activated carbons prepared from coffee residues and almond shells. It was also elucidated whether the overall adsorption rate was controlled by reaction on the adsorbent surface or by intraparticle diffusion. Experimental data of the pollutant concentration decay curves as a function of contact time were interpreted by kinetics (first- and second-order) and diffusion models, considering external mass transfer, surface and/or pore volume diffusion, and adsorption on an active site. The experimental data were better interpreted by a first-order than second-order kinetic model, and the first-order adsorption rate constant varied linearly with respect to the surface area and total pore volume of the adsorbents. According to the diffusion model, the overall adsorption rate is governed by intraparticle diffusion, and surface diffusion is the main mechanism controlling the intraparticle diffusion, representing >90% of total intraparticle diffusion.

1. Introduction

Pharmaceutical products, including metronidazole (MNZ), dimetridazole (DMZ), and sodium diatrizoate (DTZ), have been detected in ground and surface waters (Joss et al., 2006). MNZ and DMZ are antibiotics from the nitroimidazole group used in human and veterinarian medicine for the treatment of intestinal and intra-abdominal infections. Nitroimidazoles show high water solubility, low biodegradability, and elevated toxicity, being carcinogenic and mutagenic substances (Bendesky et al., 2002; Brambilla et al., 2012; Roe, 1983; Dobiáš et al., 1994; Elizondo et al., 1996). DTZ is a radiocontrast agent that is excreted unmetabolized by the human organism a few hours after its introduction; it is not completely mineralized in the environment, producing stable degradation byproducts that are more toxic than DTZ itself (Haiß and Kümmerer, 2006; Heberer, 2002; Kalsch, 1999; Pérez and Barceló, 2007). Removal of these pollutants from water systems is therefore of great importance for environment.

The removal of pharmaceutical products from water include conventional systems (chloride, chloride dioxide, wastewater treatment plants), advanced oxidation processes (AOPs) with their variants (ozone, ultraviolet radiation, gamma radiation, and electron radiation), and adsorption processes (Bendesky et al., 2002; Brambilla et al., 2012; Dobiáš et al., 1994; Elizondo et al., 1996; Haiß and Kümmerer, 2006; Heberer, 2002; Joss et al., 2006; Kalsch, 1999; Pérez and Barceló, 2007; Rivera-Utrilla et al., 2013; Roe, 1983; Sirés and Brillas, 2012). Adsorption is effective to remove organic and inorganic compounds from waters (Radovic et al., 2001), and activated carbon is one of the most widely used adsorbents for this purpose, due to its textural and chemical properties (Radovic et al., 2001). Recently, agricultural by-products have been used as precursors to synthetize low cost activated carbons standing out: coffee wastes, potato peels, coconut shells, wood, nuts, sawdust, rice hulls, bagasse and lignin.

There are reports in the literature of metronidazole (MNZ) and dimetridazole (DMZ) adsorption on different types of commercial activated carbons (Çalişkan and Göktürk, 2010; Méndez-Díaz et al.,

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Nomenclature

C_A	Concentration of solute in aqueous solution, mg/L.
C_{A0}	Initial concentration of solute in aqueous solution, mg/L.
C_{Ar}	Concentration of solute within the particle at distance r, mg/L.
$C_{Ar}\|_{r=R}$	Concentration of solute at the external surface of the particle at $r = R_p$, mg/L.
C_{Ae}	Concentration of solute at equilibrium, mg/L.
D_{AB}	Molecular diffusion coefficient at infinite dilution, cm^2/s.
D_{ep}	Pore volume diffusion coefficient, cm^2/s.
D_s	Surface diffusion coefficient, cm^2/s.
%D	Average absolute percentage deviation, %.
k_1	Rate constant of the first-order kinetic model, 1/min.
k_2	Rate constant of the second-order kinetic model, g/mg/min.
k_L	External mass transfer coefficient in liquid phase, cm/s.
m	Mass of adsorbent, g.
M_B	Molecular weight of water, g/mol.
N_{AP}	Mass transport due to pore volume diffusion.
N_{AS}	Mass transport due to surface diffusion.
q	Mass of solute adsorbed, mg/g or mmol/g.
q_{exp}	Experimental mass of adsorbate adsorbed, mg/g or mmol/g.
q_{pred}	Mass of adsorbate adsorbed predicted with the adsorption isotherms of Langmuir and Freundlich, mg/g or mmol/g.
$q_{e,1}$	Mass of adsorbate adsorbed predicted from the first-order kinetic model, mg/g.
$q_{e,2}$	Mass of adsorbate adsorbed predicted from the second-order kinetic model, mg/g.
R	Distance in radial direction of the particle, cm.
R_p	Radius of the particle, cm.
S	External surface area per mass of adsorbent, m^2/g.
T	Time, min.
V	Volume of the solution, mL.
V_A	Molecular volume of solute, cm^3/mol.

Greek symbols

η_B	Viscosity of water, cp.
ε_p	Void fraction of particles.
ρ_p	Density of adsorbent particles, g/mL.
τ	Tortuosity factor.
Ø	Association parameter of water.
ϕ_A	Dimensionless concentration of adsorbate in the solution.
ϕ_{exp}	Experimental dimensionless concentration of solute in the solution.
ϕ_{pred}	Dimensionless concentration of solute in the solution predicted with the diffusion models.

2010; Ocampo-Pérez et al., 2013; Rivera-Utrilla et al., 2009) and research data are available on sodium diatrizoate (DTZ) removal by AOPs (Velo-Gala et al., 2012, 2013) but not by adsorption. In a previous study (Rivera-Utrilla et al., 2009), the adsorption/bioadsorption of nitroimidazoles on activated carbons with different chemical and textural characteristics was investigated. The results evidenced that nitromidazoles are adsorbed on the carbon materials through dispersive interactions, moreover, they also found that the solution pH ($3 \leq pH \leq 10$) and the presence of electrolytes does not affect significantly the adsorption capacity, confirming that the electrostatic interactions are not responsible for the adsorption of these antibiotics on carbonaceous materials. Furthermore, additional results indicate that nitroimidazoles were not degraded by microorganisms. More recently, Ocampo-Pérez et al. (2013) studied the adsorption equilibrium and adsorption kinetics of MNZ and DMZ on microporous activated carbon cloth (ACC) and found that electrostatic interactions have a significant effect at $pH < 3$. Moreover, according to the kinetic models applied, the overall adsorption rate of MNZ and DMZ was governed by intraparticle diffusion.

The past two decades have seen a high demand for mesoporous carbon materials for energy storage/conversion, gas storage, and pharmaceutical release systems, thanks to their textural and chemical properties (Wang et al., 2014). Their large effective adsorption surface area also makes them highly promising materials for the adsorption of high-molecular-weight pollutants. In addition, their mesoporous structure facilitates diffusion of the pollutant within the adsorbent (Walcarius and Mercier, 2010; Qiu et al., 2014). Study of the adsorption rate and the transfer mechanism governing the adsorption process is important to support improvements in the design of continuous adsorption systems (Ocampo-Pérez et al., 2012a).

The main aim of the present investigation was to analyze the overall adsorption rate of MNZ, DMZ, and DTZ on mesoporous activated carbons prepared from coffee residues and almond shells, using kinetic and diffusion models to elucidate the diffusion mechanism governing the overall adsorption rate of these pollutants. These agricultural by-products were selected because their wide abundance reaching 6 million tons of coffee residues per year (Mussatto et al., 2011) and according to the FAO the almond shell production was around 1,162,200; 276,100 and 97,002 tons for the USA, Spain and Syria in 2009 respectively (Elleuch et al., 2013).

2. Experimental

2.1. Reagents

All reagents used in this study (MNZ, DMZ, DTZ, phosphoric acid, hydrochloric acid, sodium hydroxide) were of high-purity analytical grade supplied by Sigma–Aldrich. Table S1 (Supplementary material) exhibits the chemical structure and physicochemical characteristics of MNZ, DMZ and DTZ.

The concentration of MNZ, DMZ, DTZ inx aqueous phase was determined by high-performance liquid chromatography (HPLC) (Thermo-Scientific) equipped with a visible ultraviolet detector. A Nova-Pack C_{18} chromatographic column was used (4 μm particle size; 3.9 × 150 mm). The mobile phase for DTZ was 80% of 1% orthophosphoric acid solution v/v and 20% water at a flow of 2.0 mL min^{-1}. The mobile phase for MNZ and DMZ was 96% orthophosphoric acid solution (pH = 3–4) and 4% acetonitrile at a flow of 1.0 mL min^{-1}.

2.2. Activated carbon synthesis

Two activated carbon samples (ACA1 and ACA2) were prepared from almond shells, while ACC sample was obtained by using coffee residues. Both precursors were repeatedly washed with distilled water in order to remove dust and other inorganic impurities, then were dried in an oven at 378 K for 24 h to reduce the moisture content. Carbonization of almond shells was carried out in a furnace at 400 °C (10 °C min^{-1}) for 2 h under N_2 flow (300 cm^3 min^{-1}). A first portion of this sample was mixing with