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3D modeling of overall adsorption rate of acetaminophen on activated carbon pellets

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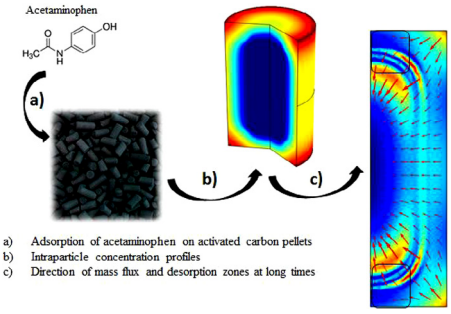
HIGHLIGHTS

- The overall adsorption rate of acetaminophen on activated carbon pellets was studied.
- 3D diffusional model was applied to predict the concentration decay curves.
- Surface and pore volume diffusion are important on the adsorption of acetaminophen.
- Desorption zones of acetaminophen were identified from 3D modeling.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work the overall adsorption rate of acetaminophen on activated carbon pellets (ACP) was analyzed in deep. The concentration decay curves were interpreted by a 3D diffusional model because the intraparticle diffusion of acetaminophen inside ACP in radial and axial directions are important in this form of activated carbon. The 3D diffusional model considers the external mass transfer, intraparticle diffusion (pore volume and surface diffusion) and the adsorption on an active site. The results demonstrated that the application of 3D diffusional model based on pore volume diffusion interprets clearly the kinetic curves, however values of effective diffusion coefficient (D_{ep}) higher than molecular diffusivity are obtained indicating superdiffusion phenomenon. On the other hand, the application of a general diffusion model evidenced that during the whole time interval, the acetaminophen diffuses consecutively by surface diffusion followed by pore volume diffusion. In short times the surface flux is higher than the pore volume flux, but at higher intervals of time, the relevance of both fluxes reverts. Finally, from 3D simulation it is clear that at longer times, the solute mainly enters from the solution through the pellet borders, and acetaminophen desorption signs are even evident at the center of the pellet covers, due to the inverse concentration gradient established between the pellet and the solution.

1. Introduction

Activated carbon (AC) is the most employed adsorbent for industrial applications, especially for eliminating aromatic compounds from water due to its physicochemical and textural properties [1]. The activated carbon is mainly commercialized in the granular (GAC), powdered (PAC), cloth, and pellets forms, and their applications depend on the required residence time, available pressure drop, capacity of regeneration, type and phase of process, and the cost of the adsorbent.

Adsorption on activated carbon has been recommended by the USA Environmental Protection Agency as the best available

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technology for removing non-biodegradable toxic organic compounds from drinking water and industrial wastewater [2], and in the last decade has been extensively used to remove pharmaceutical compounds from aqueous solutions [3–7]. From literature, it is well known that the adsorption mechanism of pharmaceutical compounds on carbonaceous materials is governed by interactions between π electron from aromatic rings of adsorbate and π electron of graphenic planes of surface of activated carbon [8–10]. Furthermore, these interactions are favored depending on the content of activating groups. Additionally, the electrostatic interactions and formation of hydrogen bond can play and important role on the adsorption of aromatic compounds [8].

To design appropriate packed adsorption columns, it is not only necessary to know the adsorption mechanism; it is also critical to obtain the adsorption rate and to identify the mass transfer mechanism that governs the overall adsorption rate. Empirical models as pseudo first order [11] and pseudo second order [12] are generally the most common kinetics models used for describing adsorption kinetics of several pollutants onto various adsorbents duo to their simplicity together with the good fit generally obtained [13–15], however, the application of these models does not provide information about the influence of operational variables on mass transfer resistances. On the other hand, the diffusional models consider the external mass transfer, intraparticle diffusion and adsorption on an active site, yielding a more realistic prediction of the phenomena [16].

We want to stress that the diffusional model is more complex when it is used to interpret experimental results. Its mathematical solution is less trivial than kinetic models, and may be it is one of the reasons for its unpopularity in the literature. As kinetic models contain empirical coefficients, then their predictive abilities under other operative conditions or scales, are diminished. The nature and physics involved in the coefficients of kinetic models is unclear, and furthermore their use for conditions different to those used in the fitted experiment is compromised [17]. Several authors have employed diffusional models to predict the adsorption rate of pollutants on activated carbon [16,18–22]. Mendez-Diaz et al. [18] investigated the adsorption kinetics of dimetridazole, metronidazole, ronidazole, and tinidazole onto activated carbon. The results evidenced that pore volume diffusion governs the adsorption process for four nitroimidazoles and the values of D_{ep} varied from 5.84×10^{-7} to 20.3×10^{-7} cm^2/s. Leyva-Ramos et al. [19] studied the adsorption rate of pentachlorophenol onto granular activated carbon, and the concentration decay data were predicted by a diffusional model which takes into account adsorption, external mass transfer, and intraparticle diffusion. The results indicated that the overall rate of adsorption is mainly controlled by surface diffusion, and the external mass transfer can be considered negligible.

In references cited above, the adsorbent particles have been considered spherical and isotropic, and, therefore, the concentration of pollutant inside the particle is only a function of time and radial position, which allows reducing the complexity of mathematical modeling. However, it is evident that these assumptions are not valid when the adsorbent particles have different shapes such as activated carbon pellets. Thus, this work aims modeling the overall adsorption rate of acetaminophen as a model compound on activated carbon pellets in aqueous solution through the application of a three-dimensional diffusional model that takes into account the external mass transport, intraparticle diffusion, and adsorption on active sites. A detailed analysis is given for the intraparticle concentration profiles and the magnitude and direction of mass fluxes over time.

Acetaminophen was selected as a model pollutant since it is one of the top prescription medicines worldwide [23]. Acetaminophen cannot be completely removed in wastewater treatment plants, and the detected residual concentrations in aqueous solutions range from several hundred ng/L to 23.2 mg/L [24]. During the chlorination processes significant amounts of acetaminophen are transformed into 1,4-benzoquinone and *N*-acetyl-*p*-benzoquinone imine increasing the toxicity of water. Furthermore, reports in the literature suggest that acetaminophen-induced hepatotoxicity was a major cause of acute liver failure in the United States and that reactive metabolites of acetaminophen may have contributed to the pathogenesis of drug-induced toxicity [25,26].

2. Experimental method and mathematical model

2.1. Adsorbate

Acetaminophen was used in this study, and was supplied by Sigma-Aldrich. The physicochemical properties of this analgesic are listed in Table 1. The concentrations of acetaminophen in aqueous solution were determined by a spectrophotometric method, and the absorbance was assessed in a double-beam, UV 2600 Shimadzu spectrophotometer. The absorbance of the acetaminophen in a water sample was measured at a wavelength of 244.1 nm.

2.2. Adsorbent

The activated carbon pellets (ACP) used in this work are distributed by Carbotecnia (Mexico), it is commercially available as Carvapur and is produced from coconut shell. The average dimensions of ACP were obtained by measuring one hundred pellets with an optical microscopy, obtaining an average diameter of 3.6 ± 0.032 mm and height of 6.5 ± 0.212 mm. The ACP were previously washed several times with deionized water, dried in an oven at 110 °C during 24 h, and stored in a plastic container.

The ACP was chemically and texturally characterized, determining their surface area, pore size distribution, solid density, void fraction, surface groups, and pH of the point of zero charge. Detailed descriptions of techniques and methods used for this characterization were previously reported [27].

2.3. Method for obtaining the adsorption equilibrium data

The experimental data for the adsorption equilibrium of acetaminophen on ACP were obtained in a batch adsorber, which consisted of a centrifugal vial of 50 mL. The procedure is described as follows: Aqueous solutions of acetaminophen were prepared in 50 mL volumetric flasks with concentrations ranging from 100 to 1000 mg/L. A portion of 10 mL of the solution was taken out from each flask to corroborate the initial concentration of acetaminophen. A certain mass of ACP and 40 mL of the acetaminophen solution were poured into the batch adsorber. Afterwards, the batch adsorber was placed in a constant temperature water bath, and the ACP and the solution were left in contact for 12 days. Once equilibrium was attained, a sample of 10 mL was withdrawn and analyzed to determine the concentration of the acetaminophen at equilibrium.

2.4. Method for obtaining the rate of adsorption data

A rotating basket batch adsorber was used to obtain the experimental concentration decay curves for the acetaminophen adsorption on ACP. This adsorber was composed of a 1 L three-neck reaction flask and an impeller with its blades replaced with stainless steel baskets. An acetaminophen solution was poured into the adsorber and the ACP particles were placed in the stainless steel mesh baskets, which were attached to a shaft connected to a variable speed motor. The adsorber was partially immersed in a constant temperature water bath controlled by a recirculator. A