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Three-dimensional mass transfer modeling of ibuprofen adsorption on activated carbon prepared by sonication

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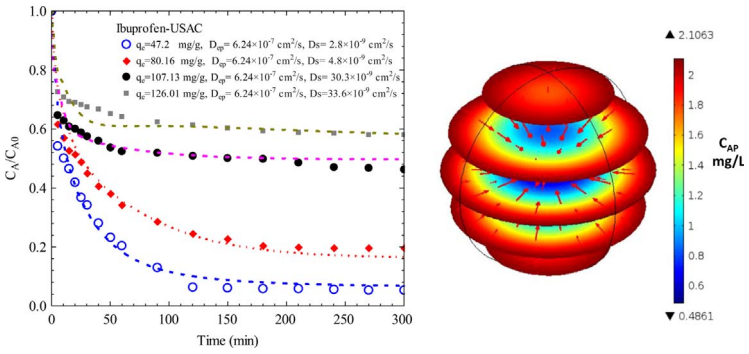
HIGHLIGHTS

- *PVSDM 3D* model was applied to ibuprofen adsorption on modified activated carbon.
- Ultrasound modification provided higher adsorption capacities for activated carbon.
- The ibuprofen molecule diffuses exclusively by surface diffusion.
- Surface diffusion coefficient values ranged from 1.8×10^{-9} to $33.6 \times 10^{-9}\,cm^2\,s^{-1}$.

GRAPHICAL ABSTRACT



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ABSTRACT

A three-dimensional mass transfer model (pore volume and surface diffusion model, *PVSDM 3D*) was applied to elucidate the ibuprofen adsorption on standard (SAC) and ultrasound modified (USAC) activated carbons. Experimental isotherms and kinetic curves were constructed at pH 2.0 and 298 K. The results revealed that USAC presented higher values of surface area, pore diameter, pore volume and void fraction than SAC, demonstrating that the ultrasonic modification was efficient to improve the characteristics of activated carbon. The adsorption capacities obtained using USAC carbon were around 25% higher in relation to the obtained using SAC carbon. For both adsorbents, the Redlich–Peterson model was able to predict the isotherm data. At pH of 2.0, dispersive interactions π–π and donor–acceptor interactions between the aromatic ring of ibuprofen and carbonyl groups of the activated carbons occurred. The concentration decay curves obtained with USAC required less time to reach equilibrium due to its modification of textural properties. The application of *PVSDM 3D* model evidenced that the D_S (surface diffusion coefficient) values for USAC were around 1.7 folds greater than those obtained by SAC, besides it was corroborated that the magnitude of total intraparticular flux is a function of time and position inside the particle. It was verified that the ibuprofen molecule diffuses exclusively by surface diffusion and that the diffusion in the pore volume can be neglected. The D_S values ranged from 1.8×10^{-9} to $33.6 \times 10^{-9}\,cm^2\,s^{-1}$.

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Nomenclature

$1/n_F$	heterogeneity factor, dimensionless
AIC	Akaike information criterion, dimensionless
ARE	Average relative error, %
a_{RP}	Affinity coefficient, $L^{\beta}\ mg^{-\beta}$
C_A	Concentration of adsorbate in aqueous solution, mg L^{-1}
C_{A0}	Initial concentration of adsorbate in aqueous solution, mg L^{-1}
C_{Ap}	Concentration of adsorbate inside the particle, mg L^{-1}
$C_{Ap}\|_{r=R}$	Concentration of adsorbate at r = R, mg L^{-1}
C_{Aexp}	Experimental values of adsorbate concentration in aqueous solution, mg L^{-1}
C_{Anum}	Predicted values of adsorbate concentration in aqueous solution, mg L^{-1}
C_e	Concentration of adsorbate at the equilibrium, mg L^{-1}
D_{AB}	Molecular diffusion coefficient at infinite dilution, $cm^2\ s^{-1}$
d	Average pore diameter of the adsorbents, Å
D_{ep}	Effective pore volume diffusion coefficient, $cm^2\ s^{-1}$
D_S	Surface diffusion coefficient, $cm^2\ s^{-1}$
k_F	Freundlich constant, (mg g^{-1}) (mg L^{-1})$^{-1/nF}$
k_L	External mass transfer coefficient, cm s^{-1}
K_L	Langmuir constant, L mg^{-1}
k_{RP}	Redlich–Peterson constant, L g^{-1}
m	Mass of adsorbent, g
N_{AP}	Mass transport due to pore volume diffusion, mg cm s^{-1} L^{-1}
N_{AS}	Mass transport due to surface diffusion, mg cm s^{-1} L^{-1}
q	Mass of adsorbate per gram of adsorbent varying with position and time, mg g^{-1}
q_e	Mass of adsorbate per gram of adsorbent at equilibrium, mg g^{-1}
q_m	Maximum adsorption capacity from the Langmuir model, mg g^{-1}
q_t	Mass of adsorbate per gram of adsorbent varying with time, mg g^{-1}
r	Position coordinate, cm
R	Adsorbent radius, cm
$R\ (\%)$	Removal percentage, %
R^2	Coefficient of determination, dimensionless
R^2_{adj}	Adjusted determination coefficient, dimensionless
S	External surface area per mass of adsorbent, $cm^2\ g^{-1}$
S_A	Specific surface area, $m^2\ g^{-1}$
$SCDP$	Surface diffusion contribution percentage, %
t	Time, min or s
V	Volume of solution, mL
V_P	Pore volume of adsorbent, $cm^3\ g^{-1}$

Greek symbols

β	Exponent of the Redlich–Peterson model, dimensionless
ε_p	Void fraction of adsorbent, dimensionless
ρ_p	Apparent density of adsorbent, g cm^{-3}
ρ_s	Solid density of adsorbent, g cm^{-3}
τ	Tortuosity of adsorbent, dimensionless
λ_{max}	Maximum wavelength of adsorbate molecule, nm
θ	C_A/C_{A0}, dimensionless

1. Introduction

In the last years, emerging contaminants such as pharmaceuticals has gained interest, since can cause adverse effects in human and wildlife, and the impact of these effects is still not quite understood. The concern of water contamination by these pharmaceutical compounds occurs because many of them are environmentally persistent, bio accumulative and endocrine disruptors [1,2]. The major causes of pharmaceutical contaminants in the environment are the large supply of medical treatments and medicines, vast accessibility, population rise and population ageing over the world. It leads to an extended discharge of pharmaceuticals in effluents, since a considerable part is eliminated unchanged into the environment by untreated and even treated sewage, once these compounds cannot be removed in the conventional treatment processes [3,4]. Among them, ibuprofen is a very common non-steroidal anti-inflammatory drug used as pain-relief. Recent studies show that ibuprofen is found in effluents, freshwater, groundwater and soil of different continents, therefore being a matter of concern [5–9].

Nowadays, there are several techniques capable of removing organic molecules from liquid matrices, such as, precipitation, air flotation, filtration, crystallization, chemical oxidation, chemical reduction, hydrolysis, reserve osmosis, adsorption, ion exchange, extraction, catalysis, among others [10,11]. Adsorption stands out because it has the advantage to be effective, economic, flexible, easy to design and to use, produces no by-products and has low-energy requirements [12,13]. An adsorption process is affected by the adsorbent's particularities, so that constantly new adsorbents and new techniques for removal contaminants are developed [14]. Activated carbon is an efficient, suitable and extensively used adsorbent [15,16]. There are several types of chemical and physical activation and the ultrasound modification technique is not much investigated. However, the ultrasound allows modification of the surface of organic materials by intense thermodynamic conditions operating at molecular level, granting new adsorption sites and increased porosity, consequently improving adsorption characteristics [17–19].

Considering new adsorbent materials, with different porous structures, like activated carbon prepared by sonication, as presented in this research, the kinetic study is a key point. Kinetic adsorption study involves mathematical models that have been suggested to interpret and elucidate the adsorption phenomena. The models are usually divided in two different classes, which are adsorption reaction models and adsorption diffusion models. The first one considers that the adsorption kinetics is entirely controlled by the adsorption rate of the solute on the surface of the adsorbent and can be expressed in the same way as the rate of a chemical reaction. The second one, the most rational manner to predict the adsorption kinetics, considers diffusion through the liquid around the adsorbent particles, diffusion in the liquid present in the pores and the pore walls and adsorption and desorption among the adsorbate and the active sites [20–22]. Although mass transfer is important to complete explain adsorption kinetics, a considerable part of the studies is based on adsorption reaction models [22–24]. Moreover, diffusion models as *PVSDM* (pore volume and surface diffusion model) are present in the literature, but they are all focused in unidirectional modeling [25–28]. The development and application of *PVSDM* in *3D* are scarce in the literature.

This work aimed to develop and apply a mass transfer model in a three-dimensional way, the pore volume and surface diffusion model (*PVSDM 3D*), to elucidate the ibuprofen adsorption onto standard and ultrasound modified activated carbons. Furthermore, a possible interaction mechanism was proposed. The activated carbons were developed by an alternative activation method (sonication) and characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), N_2 adsorption isotherms (BET), scanning electron microscopy (SEM) and other techniques. In the adsorption studies, equilibrium and kinetic curves were constructed at pH of 2.0 and temperature of 298 K. A possible interaction mechanism was proposed on the basis in the pH effect, adsorbent/adsorbate characteristics and literature. Based on this evaluation, a detailed interpretation of the mass transfer on this system