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Diffusional mass transfer model for the adsorption of food dyes on chitosan films

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ABSTRACT

The adsorption kinetics of erythrosine B and indigo carmine on chitosan films was studied by a diffusional mass transfer model. The experimental curves were obtained in batch system under different conditions of stirring rate (80–200 rpm) and initial dye concentration (20–100 mg L^{-1}). For the model development, external mass transfer and intraparticle diffusion steps were considered and the specific simplifications were based on the system characteristics. The proposed diffusional mass transfer model agreed very well with the experimental curves, indicating that the surface diffusion was the rate limiting step. The external mass transfer coefficient (k_f) was dependent of the operating conditions and ranged from 1.32×10^{-4} to 2.17×10^{-4} m s^{-1}. The values of surface diffusion coefficient (D_s) increased with the initial dye concentration and were in the range from 0.41×10^{-14} to 22.90×10^{-14} m^2 s^{-1}. The Biot number ranged from 17.0 to 478.5, confirming that the intraparticle diffusion due to surface diffusion was the rate limiting step in the adsorption of erythrosine B and indigo carmine on chitosan films.

Keywords: Biot; Chitosan films; Dyes; Diffusional model; External mass transfer; Surface diffusion

1. Introduction

Synthetic dyes, such as, erythrosine B and indigo carmine are extensively used in food processing industry to confer, intensify and restore the color of the final products (Downham and Collins, 2000). A portion of these dyes is lost during the manufacturing and processing operations, and as consequence, a considerable amount of dye–containing effluents is generated (Gupta and Ali, 2013). As reported in recent studies, the dye-containing effluents have negative direct and indirect impacts on human health and the environment, and should be carefully treated before discharge (Gupta and Suhas, 2009; Srinivasan and Viraraghavan, 2010; Verma et al., 2012). Several methods have been used to treat dye-containing effluents, such as, coagulation/flocculation (Verma et al., 2012), biosorption (Srinivasan and Viraraghavan, 2010), adsorption (Moussavi and Khosravi, 2011), bacterial decolorization (Saratale et al., 2011), advanced oxidation (Koprivanac and Kusic, 2008) and others (Koprivanac and Kusic, 2008; Gupta and Ali, 2013). It is recognized in literature that the adsorption onto chitosan is an emerging alternative technology to remove dyes from aqueous media (Crini and Badot, 2008; Wan Ngah et al., 2011).

Chitosan can be obtained from natural resources and its use as adsorbent is extremely cost effective. In addition, the adsorption capacities and adsorption rates are high (Crini and Badot, 2008). Studies have focused on chemical and physical modifications to improve the performance of chitosan as dye adsorbent (Kyzas and Lazaridis, 2009; Wan Ngah et al., 2011; Li et al., 2012; Mirmohseni et al., 2012; Zhu et al., 2012; Dotto

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Nomenclature

a_{RP}	Redlich–Peterson constant, $(\mathrm{L\,mg^{-1}})^{\beta}$
Bi_s	Biot number, dimensionless
$C(t)$	dye concentration in bulk solution, $\mathrm{mg\,L^{-1}}$
$C(x,t)$	dye concentration within the chitosan film varying with x and t, $\mathrm{mg\,L^{-1}}$
C_0	initial dye concentration in bulk solution, mg $\mathrm{L^{-1}}$.
C_e	dye concentration in bulk solution at equilibrium, $\mathrm{mg\,L^{-1}}$
$C_s(t)$	dye concentration at $x = L/2$, $\mathrm{mg\,L^{-1}}$
D_{AB}	molecular diffusion coefficient, $\mathrm{m^2\,s^{-1}}$
D_p	effective pore volume diffusion coefficient, $\mathrm{m^2\,s^{-1}}$
D_s	surface diffusion coefficient, $\mathrm{m^2\,s^{-1}}$
k_f	external mass transfer coefficient, $\mathrm{m\,s^{-1}}$
k_{RP}	Redlich–Peterson constant, $\mathrm{L\,g^{-1}}$
L	thickness of chitosan film, m or μm
m	mass of chitosan film, g
M_B	molecular weight of water, $\mathrm{g\,mol^{-1}}$
N	number of experimental points
$q(t)$	mass of dye adsorbed per gram of adsorbent, $\mathrm{mg\,g^{-1}}$
$q(x,t)$	mass of dye adsorbed varying with x and t, $\mathrm{mg\,g^{-1}}$
q_e	mass of dye adsorbed at equilibrium, $\mathrm{mg\,g^{-1}}$
q_0	mass of dye adsorbed at equilibrium with a hypothetical liquid concentration, $\mathrm{mg\,g^{-1}}$
S	external surface area per mass of adsorbent, $\mathrm{cm^2\,g^{-1}}$
t	time, min or s
T	temperature, K
V	volume of solution, L or $\mathrm{m^3}$
V_A	molar volume of solute at its normal boiling temperature, $\mathrm{cm^3\,mol^{-1}}$
x	spatial direction, m

Greek symbols

β	Redlich–Peterson constant, dimensionless
ε_p	void fraction of the chitosan film, dimensionless
η_B	viscosity of water, cp
γ	defined in Eq. (14.1)
λ_n	defined in Eq. (13.2)
ρ_p	apparent density of the chitosan film, $\mathrm{g\,L^{-1}}$
ρ_s	solid density of the chitosan film, $\mathrm{g\,L^{-1}}$
τ	tortuosity factor, dimensionless
φ	association parameter of water, dimensionless
$\psi(t)$	defined in Eq. (13.1)

et al., 2013). In this way, some chitosan based materials were developed, for example, foam (Li et al., 2012), hollow fibers (Mirmohseni et al., 2012), hydrogels (Zhu et al., 2012) and films (Dotto et al., 2013). Recently, Dotto et al. (2013) applied chitosan films to remove food dyes from aqueous solutions. Their study was focused on the equilibrium isotherms, thermodynamic and interaction analysis. However, the design of an adsorption system to treat colored effluents also requires the investigation of the adsorption kinetics (Crini and Badot, 2008). Generally, in the studies about dye removal on chitosan based materials, the kinetic investigation is based on the adsorption reaction models (Kyzas and Lazaridis, 2009; Dotto and Pinto, 2011a; Wan Ngah et al., 2011; Li et al., 2012; Mirmohseni et al., 2012; Zhu et al., 2012; Dotto et al., 2013).

The adsorption reaction models (pseudo-first order and pseudo-second order) assumes that the adsorption kinetics is exclusively controlled by the adsorption rate of the solute on the surface of the adsorbent, and the intraparticle diffusion and external mass transfer can be ignored (Ocampo-Pérez et al., 2012). Furthermore, is considered that the adsorption kinetics can be represented in the same manner as the rate of a chemical reaction (Qiu et al., 2009). Based on these models, it is not possible to obtain the mass transfer parameters and identify the rate controlling step. On the other hand, the diffusional mass transfer models are constructed on the basis of three consecutive steps: external mass transfer, intraparticle diffusion (pore volume diffusion, surface diffusion, or a combination of both mechanisms) and adsorption on an active site; and so represents more realistically the adsorption kinetics (Qiu et al., 2009; Ocampo-Perez et al., 2010, 2011; Dotto and Pinto, 2011b, 2012; Ocampo-Pérez et al., 2012). Since there are few reports in the literature about the application of diffusional mass transfer models in the adsorption of food dyes on chitosan films, detailed studies are necessary in this field.

This work aimed to develop a diffusional mass transfer model to represent the adsorption kinetics of erythrosine B and indigo carmine on chitosan films. Chitosan films were prepared and characterized by scanning electron microscopy (SEM), X-ray mapping and mechanical properties. The model was developed considering the external mass transfer and intraparticle diffusion steps, and was employed to study the experimental curves under different conditions of stirring rate and initial dye concentration. Furthermore, the mass transfer parameters were estimated and interpreted in detail.

2. Materials and methods

2.1. Dyes

The dyes used in this work were: erythrosine B (acid red 51; xanthene dye; molecular weight 879.86 $\mathrm{g\,mol^{-1}}$; C.I. 45,430; $\lambda_{max} = 526$ nm; molecular size 11.0 Å) and indigo carmine (FD&C blue no. 2; indigoid dye; molecular weight 466.34 $\mathrm{g\,mol^{-1}}$; C.I. 73,015; $\lambda_{max} = 610$ nm; molecular size 16.8 Å). These dyes (purity higher than 85%) were supplied by a local manufacturer (Duas Rodas Ind.) and were used without further purification. The chemical structures of the dyes are shown in Fig. 1. Distilled water was used to prepare all solutions. All reagents were of analytical-grade.

2.2. Preparation of chitosan films

Firstly, chitosan in powder form (deacetylation degree of 85 ± 1%, viscosity average molecular weight of 150 ± 3 kDa and particle size of 72 ± 3 μm) was obtained from shrimp wastes (*Penaeus brasiliensis*) by the following steps: demineralization, deproteinization, deodorization, deacetylation, purification and drying (Weska et al., 2007; Dotto et al., 2011a). After, chitosan films were obtained by casting technique as follows: chitosan powder was dissolved in acetic acid solution using moderate magnetic stirring (Marte, MAG-01H, Brazil) at room temperature. This solution was centrifuged (Fanem, 206 BL, Brazil) and poured onto a level plexiglas plate. Then, chitosan films were obtained by solvent evaporation and conditioned in desiccators prior to the use (Dotto et al., 2011b, 2013). More

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