Journal of Colloid and Interface Science 511 (2018) 27–38

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

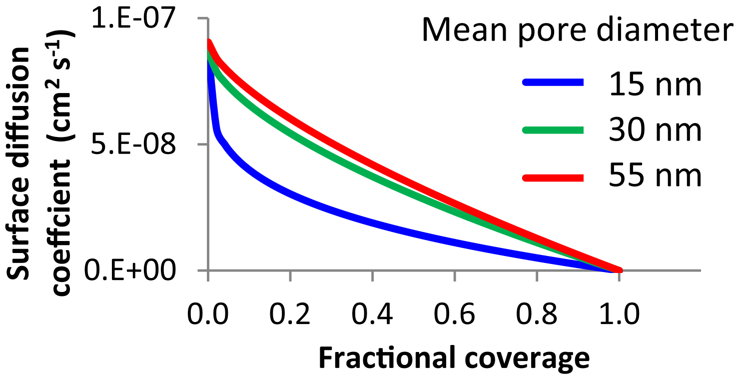
Regular Article

Load-dependent surface diffusion model for analyzing the kinetics of protein adsorption onto mesoporous materials

Gregorio Marbán *, Luis A. Ramírez-Montoya, Héctor García, J. Ángel Menéndez, Ana Arenillas, Miguel A. Montes-Morán

Instituto Nacional del Carbón (INCAR-CSIC), c/Francisco Pintado Fe 26, 33011 Oviedo, Spain

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 June 2017
Revised 7 September 2017
Accepted 23 September 2017
Available online 23 September 2017

Keywords:
Adsorption
Kinetics
Surface diffusion
Protein
Mesoporous

ABSTRACT

The adsorption of cytochrome *c* in water onto organic and carbon xerogels with narrow pore size distributions has been studied by carrying out transient and equilibrium batch adsorption experiments. It was found that equilibrium adsorption exhibits a quasi-Langmuirian behavior (a g coefficient in the Redlich-Peterson isotherms of over 0.95) involving the formation of a monolayer of cyt *c* with a depth of ~4 nm on the surface of all xerogels for a packing density of the protein inside the pores of 0.29 g cm^{-3}. A load-dependent surface diffusion model (LDSDM) has been developed and numerically solved to fit the experimental kinetic adsorption curves. The results of the LDSDM show better fittings than the standard homogeneous surface diffusion model. The value of the external mass transfer coefficient obtained by numerical optimization confirms that the process is controlled by the intraparticle surface diffusion of cyt *c*. The surface diffusion coefficients decrease with increasing protein load down to zero for the maximum possible load. The decrease is steeper in the case of the xerogels with the smallest average pore diameter (~15 nm), the limit at which the zero-load diffusion coefficient of cyt *c* also begins to be negatively affected by interactions with the opposite wall of the pore.

1. Introduction

Adsorption by porous solids in liquid phase is a process of paramount importance in the fields of water treatment, liquid-phase

---

* Corresponding author.
E-mail address: greca@incar.csic.es (G. Marbán).

https://doi.org/10.1016/j.jcis.2017.09.091
0021-9797/

separation, chromatography, etc. The modelling of liquid-phase adsorption is usually performed using well-known adsorption kinetic models [1], which allow the experimental data to be fitted in a relatively simple manner although, in many cases, they lack the theoretical basis necessary for comparing different adsorption systems. Many of the models employed are merely phenomenological, based on simple pseudo-empirical equations, and can be divided into adsorption reaction models, in which the rate determining step is the adsorption stage (i.e., pseudo-first order rate models based on the Lagergren model [2], pseudo-second order rate models [3], the second order rate model [4], and Elovich's equation [5,6]), and adsorption diffusion models, in which the kinetic process of adsorption is controlled either by liquid film diffusion [7] or by intraparticle diffusion [8–10]. Theoretical adsorption models are more complex and difficult to use in practice for fitting experimental results because the differential equations that comprise the main body of the models yield very complex and restricted analytical solutions or must be solved by means of numerical procedures. However, by applying numerical solving routines made possible by computers, realistic adsorption models, that provide a better interpretation and comparison of the fitted parameters, can be constructed so that the complicated procedure is reduced to a simple matter of personal choice.

There are a number of theoretical adsorption reaction models [11–18], based on the Langmuir [19,20] or BET [21] isotherms, (in the case study of the BET kinetic model, a simple analytical solution has only recently been found [22]), as well as theoretical adsorption diffusion models, based on Fick's second law. The adsorption diffusion models [23–29] are differentiated by the possible combinations of the three diffusion steps that govern the overall process: (i) liquid film diffusion, (ii) pore diffusion and (iii) surface diffusion. An adsorption system in which adsorption diffusion is known to be the rate determining step is one which involves the recovery, purification or immobilization of proteins through ion-exchange, adsorption chromatography or porous-particle adsorption [30–32]. This process has usually been described by using four types of adsorption diffusion models: (i) the pore diffusion model, where the driving force for intraparticle mass transfer is the protein concentration gradient in the pore phase, with no surface diffusion [28,31], (ii) the surface diffusion model, in which surface diffusion is the rate-limiting step in the adsorption process [33], (iii) the homogeneous diffusion model, which considers each adsorbent particle as a homogeneous network, and the driving force for protein diffusion is the total protein concentration gradient within the adsorbent [34,35] and (iv) the parallel diffusion model, which assumes that pore and surface diffusion occur at the same time in an adsorbent particle [36,37]. In a work by Chen et al. [38] the four models were solved by an orthogonal collocation method, under the assumption that external liquid-film mass transfer resistance was negligible and then used to fit the experimental curves of the adsorption kinetics of bovine serum albumin (BSA) and γ-globulin to an anion exchanger. They found that the parallel diffusion model provided the best fit for the experimental data.

An important feature of standard pore and surface diffusion models which is often ignored is that the diffusion coefficients are always independent of the spatial coordinates. This simplifies enormously the task of numerically resolving the mass balances. Thus, in the classical homogeneous surface diffusion model by Mathews, Weber and Walter [24–26] that employs spherical coordinates, in the intraparticle mass balance expressed by Eq. (1), the surface diffusion coefficient is always treated as a constant and Eq. (1) can be transformed into the more easily solvable Eq. (2);

$$\frac{\partial q(r,t)}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_S \frac{\partial q(r,t)}{\partial r}\right) \tag{1}$$

$$\frac{\partial q(r,t)}{\partial t} = D_S\left(\frac{2}{r}\frac{\partial q(r,t)}{\partial r} + \frac{\partial^2 q(r,t)}{\partial r^2}\right) \tag{2}$$

where q(r, t) is the amount of adsorbate adsorbed onto the surface of the porous particle (mg g^{-1}) at the radial position r (cm) and at time t (s) and D_S ($cm^2\ s^{-1}$) is the surface diffusion coefficient or surface diffusivity. However, to assume that surface diffusivity is independent of the radial coordinate is a disputable point [39]. According to the HIO theory of Higashi et al. [40], which is based on the random displacement of molecules between adsorption sites on a solid surface, the transition time between sites is negligible when compared to the residence time on each site, and the molecule jumps across immediately when it encounters a site already occupied by another molecule. From this theory, Kapoor and Yang [39] derived the following expression for the spatial-dependent surface diffusivity:

$$D_S(r,t) = \frac{D_0}{1-\theta(r,t)} \tag{3}$$

where D_0 is the diffusion coefficient at zero coverage and θ(r, t) is fractional surface coverage, q(r, t)/q_m, q_m being the maximum amount of adsorbate loaded by the particle in mg g^{-1}. Later it was proved that Eq. (3) was a specific case covered by the general model for surface diffusion of gases in porous solids formulated by Chen and Yang [41,42], this particular case corresponding to the absence of blockage in the channel opening. This model predicts an initial increase in the diffusion coefficient up to coverages close to a monolayer and its subsequent decrease due to multilayer condensation. Other authors take into consideration the affinity between adsorbed molecules. For instance, Zhdanov [43] suggests the use of the following empirical equation:

$$D_S(r,t) = D_0 \times e^{\alpha\times\vartheta(r,t)} \tag{4}$$

where parameter α is positive for repulsive and negative for attractive lateral interactions between adsorbed particles. Whereas Eq. (3) has been proved to be valid for gases at low degrees of coverage, whether bulky proteins behave similarly when adsorbed on a solid surface is open to dispute. For instance, Tilton et al. [33] found a significant hindrance of surface diffusion that increases with increasing surface concentration, owing to interactions between the adsorbed proteins. In that case parameter α of Eq. (4) should present a negative value. However, no kinetic model for the adsorption (either of proteins or of any other adsorbate) onto porous solids that considers the dependence of the diffusion coefficient on the surface coverage has ever been fully solved.

In the present work we propose and solve a load-dependent surface diffusion model for protein adsorption that follows Fick's second law in which (a) surface diffusivity depends on surface coverage (load) via a new empirical relation and (b) external liquid-film mass transfer resistance is considered. The model has been tested in the adsorption of cytochrome *c* onto mesoporous organic and carbon xerogel particles synthesized by means of microwave heating [44–46].

2. Load-dependent surface diffusion model (LDSDM)

This model is a variation of the homogeneous surface diffusion model (HSDM) initially proposed by Mathews, Weber and Walter [24–26] and later simplified by the *Linear driving force* approximation [27]. The HSDM assumes that the surface of adsorbent particles is homogeneous and that the adsorbate is transferred from one adsorption site to an inner adsorption site inside the particles, according to Fick's second law [25]. In the HSDM, the diffusion coefficient is considered to be independent of the amount of adsorbate in the sorbent (load) at any time, whereas the present model