



Critical analysis of adsorption/diffusion modelling as a function of time square root



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HIGHLIGHTS

- Detailed development of models for intraparticle mass diffusion.
- Definition of conditions that validates adsorption as function of time square root.
- Critical analysis of the quality of the time square root approach.
- Evaluation of external mass transfer resistance in time square root plots.
- Critical analysis of the multilinear segments in time square root plots.

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ABSTRACT

A very common procedure to evaluate intraparticle diffusion in batch adsorption experiments consists in plotting the adsorbed concentration versus the square root of time. Furthermore, some works present in this plot a sequence of linear sections, attributing a specific phenomenon to each one, such as external mass transfer resistance and intraparticle diffusion into pores of different sizes. In spite of this frequent approach, the mathematical foundations of this relationship are rarely presented. In this work, it is presented a complete description of the physical-chemical and mathematical basis that leads to the relationship between adsorbed quantity and time square root, evincing the necessary hypotheses for this relationship to become meaningful. It was observed that this relationship could only be applied within very restrictive conditions: adsorption in a semi-infinite solid and constant liquid phase concentration. Moreover, this relationship is strictly valid in the absence of external mass transfer resistance, for linear adsorption isotherm and instantaneous equilibrium of fluid and solid concentrations inside the pores. It is clear that these restrictions are scarcely achieved under usual batch adsorption experiments. Besides, multilinear plots used to differentiate among external diffusion and macro, micro and mesoporous diffusion are evidently shown to be very subjective and without any mathematical support.

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1. Introduction

Adsorption of species from a liquid solution into a porous solid comprises a sequence of steps. Initially, (i) mass is transferred from bulk liquid phase through boundary film to solid external surface. Then, (ii) mass is transferred into the solid pores by in series or in parallel liquid phase diffusion and surface diffusion (Costa and Rodrigues, 1985). The last step, (iii) consist in the kinetics of mass

transfer from liquid phase onto solid surface inside pores. The first step is also known as external film diffusion, the second step is the intraparticle diffusion and the third step consists of the adsorption step which includes both adsorption kinetics and adsorption equilibrium, usually described as an adsorption isotherm.

In many cases, intraparticle diffusion can be considered much slower than the other steps, particularly with respect to the adsorption kinetic inside particle pores. In this case, it is assumed that equilibrium between fluid and surface concentrations are instantaneously reached inside the pores, and the kinetic of adsorption can be just described by mass transfer processes.

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Therefore, a very common way to evaluate intraparticle diffusion consists in plotting the adsorbed quantity versus square root of time. This relationship is referenced as “Weber and Morris Intraparticle Diffusion Model” due to Weber and Morris (1963) work about adsorption kinetics onto activated carbon, although the mathematical foundations are usually credited to Crank (1975). Weber and Morris (1963) had also cited Edeskuty and Amundson (1952), where some plots of the adsorbed quantity versus time square root are used, but even the work of Boyd et al. (1947) already had presented this relationship, considering diffusion into a semi-infinite solid.

Mathematically, this simple correlation is represented by Eq. (1), where the adsorbed quantity, q_t , varies linearly as a function of the square root of time t .

$$q_t = k_{id}\sqrt{t} + C \quad (1)$$

In Eq. (1), k_{id} is the intraparticle diffusion rate constant and C represents the boundary effect. Some works state that when constant C is null only intraparticle diffusion is the controlling step; otherwise, there are other mass transfer mechanisms along with intraparticle diffusion in the adsorption process (Chen and Zhang, 2014; Shi et al., 2013). It is also affirmed that constant C value gives an idea about the thickness of the boundary layer; and the larger the constant C value is, the greater is the boundary layer effect (Ahmad and Rahman, 2011; Mahmoud et al., 2012; Shi et al., 2013; Srivastava et al., 2006).

In the literature, a sequence of linear sections when q_t is plotted as a function of $t^{1/2}$ is also commonly presented. The occurrence of this multilinearity is attributed to the presence of two or more mass transfer mechanisms that control the adsorption process. For instance, some works (Albadarin et al., 2011; Allen et al., 1989; Cheung et al., 2007) ascribe to each linear section the diffusion in pores of gradually smaller sizes, that is, macropores, mesopores and micropores. Some works also assign to the initial linear section the resistance to external mass transfer (Chen and Bai, 2013; Koumanova et al., 2003), followed by a second step where intraparticle diffusion is rate limiting and finishing with a slower step due to approach to equilibrium (El-Khaiary and Malash, 2011; Cheung et al., 2007). Ahmad and Rahman (2011) had attributed a strong electrostatic attraction between dye and the external surface of adsorbent that results into the first sharper region.

On the other hand, just a few works attempt to establish the mathematical foundations of Equation (1). Some papers (Choy et al., 2004; Koumanova et al., 2003; Qiu et al., 2009; Srivastava et al., 2006; Walker et al., 2003) presented that this model consider the initial concentration in the solid is null; while radial diffusion and external mass transfer resistance are significant just in the beginning of the process.

It is valuable to note that kinetic selectivity of rate based separations, as in some pressure swing adsorption processes that are kinetically controlled, are defined under assumption of adsorption of each adsorbate being proportional to the square root of time (Ruthven et al., 1994; Yang, 1997).

The primary objective of this work is to present a complete description of the physicochemical phenomena and the mathematical basis that leads to the relationship between adsorbed quantity and square root of time, clearly exposing the necessary hypotheses for this correlation to become meaningful. Simulated data are used to evaluate the adsorption kinetics, showing evidently the weaknesses of this approach. Finally, multilinear plots of adsorbed quantity are shown to be very arbitrary and without any mathematical foundation that could support such procedure.

2. Mathematical modelling

Mass transfer inside a porous solid particle is described mathematically by a partial differential equation that determines how solute concentration varies as a function of time and space. Under some hypotheses, this partial differential equation can be written in a dimensionless form according to Eq. (2), where C_p is solute concentration in the fluid phase inside the particle, τ is dimensionless time defined in Eq. (3), η is dimensionless spatial variable defined in Eq. (4) and S is a constant that defines the particle geometry: 0 for a slab, 1 for a cylinder and 2 for a sphere.

$$\frac{\partial C_p}{\partial \tau} = \frac{1}{\eta^S} \frac{\partial}{\partial \eta} \left(\eta^S \frac{\partial C_p}{\partial \eta} \right) \quad (2)$$

$$\eta = \frac{r}{R} \quad (3)$$

$$\tau = \frac{D_{app}}{R^2} t \quad (4)$$

R is the radius for cylindrical and spherical particles and is the half thickness of the slab particle. D_{app} is the apparent diffusivity and considers two diffusion coefficients, fluid and surface diffusivities, D_p and D_s , the particle porosity ε , solid density, ρ_s , and slope of the equilibrium isotherm equation, K , (Do, 1998), as defined in Eq. (5). Detailed development of this model can be found in the Supplementary Material.

$$D_{app} = \frac{\varepsilon D_p + (1 - \varepsilon) \rho_s K D_s}{\varepsilon + (1 - \varepsilon) \rho_s K} \quad (5)$$

In order to solve Eq. (2), an initial condition is necessary, and since it is usually used a new clean sample of solid adsorbent in every experimental run, the initial solute concentration inside particle is zero, Eq. (6).

$$C_p|_{\tau=0} = 0 \quad (6)$$

Two boundary conditions are needed. At the particle center, r or η equal to zero, the symmetry condition is considered, Eq. (7).

$$\frac{\partial C_p}{\partial \eta} |_{\eta=0} = 0 \quad (7)$$

Usually it can be defined two different kinds of boundary condition at external particle surface, that is, at r equal to R or η equal to 1. The first one, Eq. (8), defines that solute concentration at particle outside boundary is equal to the fluid bulk concentration, *i.e.*, there is no mass transfer resistance outside the particle. The second option, Eq. (9), defines that the external mass transfer resistance is not negligible, and a boundary layer is present around solid particles. In Eq. (9), Bi_m is the Biot number for mass transfer, which is the ratio between internal and external mass transfer resistances, as defined in Eq. (10), where k_m is the convective mass transfer coefficient.

$$C_p|_{\eta=1} = C_B \quad (8)$$

$$-\frac{\partial C_p}{\partial \eta} |_{\eta=1} = Bi_m (C_p|_{\eta=1} - C_B) \quad (9)$$

$$Bi_m = \frac{k_m R}{D_{app} [\varepsilon + (1 - \varepsilon) \rho_s K]} \quad (10)$$

2.1. Infinite Bath Approach (IBA)

For both kinds of external boundary conditions, Eqs. (8) and (9), particularly when D_{app} and C_B can be considered constants,

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