Analysis of commonly used batch adsorption kinetic models derived from mass transfer-based modelling

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Abstract

Modelling of liquid–solid batch adsorption based on mass transfer and conservation equations results in differential equations that may have or not an analytical solution. Even when analytical solutions are available, several simplified models can be considered for evaluating kinetic data of batch adsorption experiments. However, these simplified models are commonly used regardless of the premises considered in its development, and the analysis of the kinetic experiments based on these simplified models may be severely compromised. For this reason, this work presents a detailed development of the phenomenological models, and the hypotheses considered in its development are clearly stated. Typical simplified models derived from the phenomenological ones are obtained, and the conditions considered in the simplification are critically assessed. It was observed that the simplified models fail mainly for considering the concentration of the bulk phase constant over time or considering a linear adsorption isotherm. It must be emphasised that even when phenomenological models must be solved through numerical procedures, its use must be preferred, since the agreement with model premises and experimental conditions are closer, ensuring the quality of the kinetic data analysis.

Keywords Adsorption kinetics · Batch adsorption · Liquid–solid adsorption · Mass transfer · Phenomenological models · Simplified kinetic models

Introduction

Adsorption is a separation technique widely used in water and effluent treatment processes (Gupta and Suhas 2009; Fallou et al. 2016). The commonly used adsorbents include activated carbon, zeolites, silica, ion exchange resins and some other low-cost materials (Ruthven 1984; Do 1998; Gupta and Suhas 2009). The understanding of the

equilibrium and kinetics of the adsorption process is essential for evaluation and comparison of different adsorbents, providing information about the adsorption capacity and time required to reach equilibrium. Additionally, obtaining information on performance and mechanisms that are occurring during the adsorption process is also an important step to evaluate an adsorbent (Qiu et al. 2009).

Several models were developed to describe the processes that occur in adsorption. These models are usually based on phenomenological principles using conservation equations, equilibrium relation and mass transport equations, as the homogeneous surface diffusion model (HSDM), pore volume diffusion model (PVDM) and pore volume and surface diffusion model (PVSDM) (Roy et al. 1993; Leyva-Ramos and Geankoplis 1994; Lyn 1996; Souza et al. 2017). The mass transfer phenomenon comprises a sequence of steps: (i) The mass is transferred from the bulk phase through the stagnant liquid film around the adsorbent particle to its external surface (convective external mass transfer); (ii) the intraparticle diffusion of the solute within the adsorbent

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porous that can happen by diffusion in the fluid phase confined in the particle porous and by surface diffusion of the adsorbed molecules of solute; and (iii) adsorption of solute from fluid phase in the particle porous to the porous surface (this is the actual adsorption step) (Malash and El-Khaiary 2010; Yao and Chen 2015, 2017; Schwaab et al. 2017).

Any single step or combination of these steps can be defined as the process control mechanism. In porous materials, the adsorption step is typically much faster than the mass transfer steps, and it is usually assumed that the porous fluid phase and surface phase concentrations are locally at equilibrium (Malash and El-Khaiary 2010; Yao and Chen 2017).

When intraparticle diffusion is considered, the phenomenological approaches lead to a partial differential equation for prediction the concentration profile as a function of particle length and time. This equation only has analytical solution when kinetics of adsorption inside particle porous (step iii) are considered at equilibrium (a reasonable hypothesis) and the equilibrium is well described by a linear adsorption isotherm; that is, it follows the Henry Law. This last assumption is only valid when concentrations are low inside adsorbent particle, as it is in the beginning of the batch adsorption experiment. Otherwise, this is not a reasonable assumption since nonlinearity of the adsorption isotherm must be considered. In this case, the model equations do not have an analytical solution and must be solved with the help of numerical procedures (Silva et al. 2014; Schwaab et al. 2017; Souza et al. 2017).

In order to avoid the numerical solution of the partial differential equations (Digiano and Weber 1973; Letterman et al. 1974; Yao and Chen 2015), simplified procedures and models are commonly used, although the conditions considered for simplification of the solution are not usually compatible to the conditions of the experimental setup.

For this reason, the objective of this study is to review the development of phenomenological models, with special attention to the initial and boundary conditions considered to solve model equations and other additional premises (usually considered to allow model solution or simplification), with special attention in the reliability of these conditions and assumptions for applications in the analyses of batch adsorption experiments. It will be shown that the conditions considered in the development and simplifications of the models are generally not in good agreement with the conditions typically found in batch adsorption experiments. Since these simplified models are typically used for estimation of mass transfer parameters and evaluation of the adsorption/mass transfer principal mechanism, one can argue if these simplified models, based on unreasonable assumptions, are adequate for the analysis of kinetic data of batch adsorption. Finally, it is emphasized that the use of numerical procedures for solution of partial differential equations is nowadays available in many software and different computational languages and its use must be preferred since the conditions considered can be much closer to the actual experimental ones, improving the analysis quality of batch adsorption experimental data.

Intraparticle mass transfer model

This section is focused on derivation of phenomenological models based on intraparticle mass transfer for liquid–solid adsorption in batch systems. The adsorbent particle is considered porous, and the mass transfer flux inside particle is described by the Fick law in the pore space and in the adsorbed phase; that is, pore and surface diffusion are considered. Initially, it is presented a mass balance in the adsorbent particle and some analytical solutions when the batch adsorber is considered an infinite bath, that is, with concentration of the liquid bulk phase constant over time. Then, it is presented the mass balance of the liquid bulk phase that is needed for considering the batch adsorber as a finite bath with its concentration varying over time.

Mass balance in the adsorbent particle

Adsorbents are usually composed by solid porous particles. Inside these particles, a single adsorbate in a liquid phase, for instance, can be transferred through pore phase and surface diffusion. Although there are some complex models that consider separated mass transfer equations for macropore and micropore particle regions (Ruthven 1984; Do 1998; Inglezakis et al. 2018) or variable diffusivity (Inglezakis et al. 2019), the scope of this paper is to discuss the common simplified models used in the literature. Furthermore, Lagergren pseudo first and second order models (Ho and McKay 1999; Ho 2004; Tien and Ramarao 2014; Rodrigues and Silva 2016), Elovich model (Turner 1975; Chien and Clayton 1980; Largitte and Pasquier 2016) and kinetic models based on Langmuir adsorption/desorption rate (Ho et al. 2000; Largitte and Pasquier 2016; de Assis Filho et al. 2021) were not considered in this work, since these models are not based on mass transfer phenomenon.

Then, considering a homogenous porous particle, an unidimensional mass balance leads to Equation (1) (Do 1998), where the two terms in the left side describes the time variation of the concentrations in the pore fluid phase C_p and on the solid surface q, and (Do 1998) the two terms in the right side described the mass transfer by pore and surface diffusion, respectively. Besides, D_p and D_s are the porous and surface diffusivities, that are considered constant, t is the time, r is the spatial distance in the particle, and S is the particle shape factor, that is equal to 0, 1 and 2 for slab, cylinder and sphere, respectively. Finally, ε is the particle

porosity and ρ_p is the particle density, that is related to the solid density ρ_s, according to $\rho_p = \rho_s(1 - \varepsilon)$.

$$\varepsilon \frac{\partial C_p}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \varepsilon \frac{D_p}{r^S} \frac{\partial}{\partial r}\left(r^S \frac{\partial C_p}{\partial r}\right) + \rho_p \frac{D_s}{r^S} \frac{\partial}{\partial r}\left(r^S \frac{\partial q}{\partial r}\right) \quad (1)$$

The second term in the left side of Equation (1) can be seen as the actual rate of adsorption. As briefly discussed in the "Introduction" section, the rate of mass transfer by diffusion is usually much slower than the adsorption rate, and it is reasonable to consider that concentrations in the fluid phase inside particle pores are at equilibrium with concentration on the pore surface. Since these concentrations at equilibrium are usually related to each other by an adsorption isotherm, it can be written that q is a function of C_p and its variation as a function of time t and space r can be written according to Equation (2), where x stands for t or r:

$$\frac{\partial q}{\partial x} = \frac{\partial q}{\partial C_p} \frac{\partial C_p}{\partial x} \quad (2)$$

Substituting Equation (2) into Equation (1) leads to Equation (3). It must be observed that the derivative $\partial q/\partial C_p$ is usually an implicit function of spatial variable r and when the last term of Equation (3) is expanded through the differentiation, a second order derivative appear, that is, $\partial^2 q/\partial C_p^2$. This expansion will not be shown here since it is not necessary for the development of the simplified models usually considered in the literature, although it is an important observation to be done, especially when nonlinear isotherms are considered (Do 1998; Souza et al. 2020).

$$\varepsilon \frac{\partial C_p}{\partial t} + \rho_p \frac{\partial q}{\partial C_p} \frac{\partial C_p}{\partial t} = \varepsilon \frac{D_p}{r^S} \frac{\partial}{\partial r}\left(r^S \frac{\partial C_p}{\partial r}\right) + \rho_p \frac{D_s}{r^S} \frac{\partial}{\partial r}\left(r^S \frac{\partial q}{\partial C_p} \frac{\partial C_p}{\partial r}\right) \quad (3)$$

When adsorption isotherm is well described by a liner equation, that is, follows the Henry law, the derivative of q with respect to C_p is a constant K, as shown in Equation (4), and Equation (3) can be rewritten as Equation (5), where D_{app} is the apparent diffusivity defined in Equation (6) that takes into account both porous and surface diffusivities, equilibrium constant and porosity and density of particle.

$$\frac{\partial q}{\partial C_p} = K \quad (4)$$

$$\frac{\partial C_p}{\partial t} = D_{app} \frac{1}{r^S} \frac{\partial}{\partial r}\left(r^S \frac{\partial C_p}{\partial r}\right) \quad (5)$$

$$D_{app} = \frac{\varepsilon D_p + \rho_p K D_S}{\varepsilon + \rho_p K} \quad (6)$$

The definition of the apparent diffusivity in Equation (6) shows that it has a weighted contribution of both porous and surface diffusivities, and this model is then called a pore volume and surface diffusion model, PVSDM; when surface diffusion can be neglected, D_s is assumed to be null, and the model is called pore volume diffusion model, PVDM; on the other side, when diffusion in the porous of the particle can be neglected, that is D_p and/or ε is null, apparent diffusivity is equal to surface diffusivity, and the model is called surface diffusion model, SDM, or homogeneous surface diffusion model, HSDM (Do and Rice 1987; Roy et al. 1993; Ocampo-Pérez et al. 2013; Viegas et al. 2014).

Equation (5) is a partial differential equation for its an initial condition, Equation (7), and two boundary condition, Equations (8) and (9), are necessary. The initial condition defines a uniform initial concentration inside particle pores, and, since it is usually used a fresh adsorbent, this value is commonly equal to zero. Boundary condition in the particle centre, that is, at r equal to 0, is the symmetry condition. In Equation (9), k_m is the convective mass transfer coefficient in the stagnated liquid film surrounding the adsorbent particle, and C_b is the concentration of the liquid bulk phase of the batch adsorber. This condition states the boundary condition at the external particle surface, that is, at r equal to R, and is defined by equalling the flux of mass transfer by convection from the liquid bulk phase to the external particle surface, with the flux of mass transfer by pore volume and surface diffusion.

$$C_p\Big|_{t=0} = 0 \quad (7)$$

$$\frac{\partial C_p}{\partial r}\Big|_{r=0} = 0 \quad (8)$$

$$-\left(\varepsilon D_p + \rho_p K D_s\right) \frac{\partial C_p}{\partial r}\Big|_{r=R} = k_m\left(C_p\Big|_{r=R} - C_b\right) \quad (9)$$

An important dimensionless number that arises from the boundary condition at the external particle surface is the Biot number and is defined as.

$$Bi = \frac{k_m R}{\varepsilon D_s + \rho_p K D_s} \quad (10)$$

The Biot number is the ratio between the internal to external resistances to mass transfer. Considering that batch adsorption experiments are usually performed with small adsorbent particles and in well agitated baths, Biot number tends to be very high (in fact, it usually tends to infinity), and the external resistance to mass transfer can be neglected, leading the boundary condition at the external particle surface to be simplified to:

$$C_p\big|_{r=R} = C_b \tag{11}$$

In this way, under the assumption of constant pore volume and surface diffusivities and, principally, considering that the adsorption equilibrium is well described by a linear adsorption isotherm, the mass transfer model for a porous solid adsorbent is described by Equation (5), together with initial and boundary conditions defined in Equations (7), (8) and (9) or (11).

Analytical solutions for infinite bath

The partial differential equation can be solved analytically, and this solution provides the concentration inside adsorbent particle as a function of time and position. However, the major interest usually is not in the concentration profile inside particle, but in the total adsorbate removal. This value is closely related to the average concentration inside particle, $\overline{C}_p$, that can be related to the fractional uptake, F, according Equation (12) (Do 1998; Schwaab et al. 2017). According to this equation, at time equal zero, fractional uptake is null, since bulk concentration is equal to its initial value C_{b0} and also in accordance to the initial condition in the particle, Equation (7); by the other side, when the average concentration inside particle reaches the concentration in the liquid bulk phase, C_b, fractional uptake is equal to 1.

$$F(t) = \frac{C_{b0} - C_b(t)}{C_{b0} - C_{b,eq}} = \frac{\overline{C}_p(t)}{C_{p,eq}} = \frac{\overline{q}(t)}{q_{eq}} \tag{12}$$

It is important to point out that this definition considers that bulk concentration can vary over time that characterizes a finite bath system. However, when an infinite bath system is considered, C_b is constant over time. Then fractional uptake is computed according to Equation (13), that is the ratio between average concentration inside particle, and its maximum value, that is equal to C_b, or the ratio between the average concentration on the solid surface and its maximum value, that is equal to product KC_b.

$$F(t) = \frac{\overline{C}_P(t)}{C_b} = \frac{\overline{q}(t)}{KC_b} \tag{13}$$

Using the method of separation of variables, a general solution can be written for the three classical geometries (Crank 1975; Do 1998; Schwaab et al. 2017) as a function of the shape factor S, according to Equation (14), where τ is the dimensionless time, also known as the Fourier number, and is defined in Equation (15):

$$F = 1 - 2(S+1) \sum_{n=1}^{\infty} \frac{1}{\gamma_n^2} \frac{Bi^2}{\left(\gamma_n^2 + Bi^2 + (1-S)Bi\right)} exp\left(-\gamma_n^2\tau\right) \tag{14}$$

Table 1 Characteristic values or equations for the three typical geometries

	Shape	Characteristic values or equations
Negligible external mass transfer resistance	Slab	$\gamma_n = (2n-1)\frac{\pi}{2}$
	Cylinder	$J_0(\gamma_n) = 0$
	Sphere	$\gamma_n = n\pi$
Considerable external mass transfer resistance	Slab	$\gamma_n tan(\gamma_n) = Bi$
	Cylinder	$\gamma_n J_1(\gamma_n) = Bi\, J_0(\gamma_n)$
	Sphere	$\gamma_n cot(\gamma_n) = 1 - Bi$

Table 2 Solutions obtained with the Laplace transform method for infinite bath with negligible external resistance to mass transfer (Schwaab et al. 2017)

Shape	Solution
Plane	$F = 2\sqrt{\tau}\{\frac{1}{\sqrt{\pi}} + 2\sum_{n=1}^{\infty}(-1)^n \mathrm{ierfc}(\frac{n}{\sqrt{\tau}})\}$
Cylinder	$F = 4\frac{\sqrt{\tau}}{\sqrt{\pi}} - \tau - \frac{1}{3\sqrt{\pi}}\sqrt{\tau^3} + \cdots$
Sphere	$F = 6\sqrt{\tau}[\frac{1}{\sqrt{\pi}} + 2\sum_{n=1}^{\infty}\mathrm{ierfc}(\frac{n}{\sqrt{\tau}})] - 3\tau$

$$\tau = \frac{D_{app}t}{R^2} \tag{15}$$

When external resistance to convective mass transfer is negligible, Biot number tends to infinite, and Equation (14) is rewritten according to the Equation (16):

$$F = 1 - 2(S+1) \sum_{n=1}^{\infty} \frac{1}{\gamma_n^2} exp\left(-\gamma_n^2\tau\right) \tag{16}$$

In Equations (14) and (16), the values of γ_n are the positive roots of characteristic equations defined in Table 1. When external resistance to mass transfer is negligible, these characteristic equations have analytical solutions for plane and spherical geometries.

Although these analytical solutions involve a sum of infinite terms, these series usually converges rapidly when dimensionless time τ is high, and only the first term of these solutions is necessary to provide reasonable predictions.

By the other side, these solutions converge slowly for low values of τ, and alternative solutions should be considered. These solutions can be obtained with the Laplace transform method (Crank 1975; Albadarin et al. 2011; Schwaab et al. 2017) and are presented in Table 2, only considering the case with negligible external resistance to mass transfer these. It must be pointed out that solutions for plane and spherical geometries can be presented in a closed analytical form, but

for cylindrical geometry, only an open and approximated solution could be developed (Schwaab et al. 2017).

At this point, it is important to notice that the solutions presented in this section are strictly valid only for infinite baths where bulk concentration remains constant over time and considering a linear adsorption isotherm. Furthermore, some solution are only valid for negligible external resistance to mass transfer, that is, when Biot number tends to infinite and concentration at external particle surface is equal to the Bulk concentration, according to the boundary condition presented in Equation (11).

Analytical solutions for finite bath

When bulk concentration decreases significantly, an infinite bath approach can not be considered and a mass balance equation for the bulk phase must be considered, according Equation (17). This equation must be solved simultaneously with Equation (3), that is, the mass balance in the solid adsorbent particle. In this case, any adsorption isotherm can be considered, but the solution generally only is obtained through numerical procedures (Do 1998; Schwaab et al. 2017; Souza et al. 2017).

$$\frac{dC_b}{dt} = \frac{M}{V\rho_p} r_b \tag{17}$$

In Equation (17), M is the adsorbent mass, V the volume of the bulk phase, and r_b is the rate of mass transfer from the bulk phase to the interior of the particles (the value of r_b is negative in the adsorption process, since bulk concentration decrease over time). This rate is closely related with the boundary condition defined in Equation (9). Then, this rate can be defined with respect to the convective mass transfer from bulk phase to the external surface of particles or with respect to the diffusive mass transfer from the external surface of particles into the particle, according to Equations (18) and (19), respectively. In both equations, $(S+1)/R$ is the ratio of external surface area to volume (A_p/V_p) of each particle shape, and J_{conv} and J_{dif} are the convective and diffusive mass transfer fluxes at the external particle surface (both values are negative in the adsorption process).

$$r_{b,con} = \frac{A_P}{V_P} J_{conv} = \frac{(S+1)}{R} k_m(C_p|_{r=R} - C_b) \tag{18}$$

$$r_{b,dif} = \frac{A_P}{V_P} J_{dif} = \frac{(S+1)}{R}[-(\varepsilon D_p + \rho_p D_s K)\frac{\partial C_p}{\partial r}|_{r=R}] \tag{19}$$

Both Equations (18) or (19) can be inserted into Equation (17), and, also considering Equations (6) and (10), one

may obtain Equations (20) and (21). Particularly in Equation (21), η is a dimensionless spatial variable, defined as $\eta = r/R$:

$$\frac{dC_b}{d\tau} = \xi(S+1)Bi(C_p|_{r=R} - C_b) \tag{20}$$

$$\frac{dC_b}{d\tau} = -\xi(S+1)\frac{\partial C_p}{\partial \eta}|_{\eta=1} \tag{21}$$

In Equations (20) or (21), ξ is the mass capacity factor (Rodrigues and Silva 2016), a constant defined according to Equation (22). When ξ tends to zero, this finite bath model will lead to similar results obtained with the infinite bath models presented in the previous section.

$$\xi = \frac{(M/\rho_p)(\varepsilon + \rho_p K)}{V} \tag{22}$$

Once again, if the adsorption isotherm is linear, analytical solution can be obtained through Laplace transform (Crank 1975). For the case without external resistance to mass transfer, solutions can be concisely written according to Equation (23), with γ_n the roots of characteristic equations presented in Table 3. Sometimes, in these solutions, it is considered the constant α (Crank 1975) that is the inverse of the mass capacity factor ξ, defined in Equation (22).

$$F = 1 - \sum_{n=1}^{\infty} \frac{2(S+1)(1+\xi)}{\gamma_n^2 + \xi(1+\xi)(S+1)^2} \exp(-\gamma_n^2\tau) \tag{23}$$

General solutions for the finite bath model considering a linear adsorption isotherm can be developed. These solutions consider the cases with significant and negligible external resistance to mass and are based on generic Bessel functions that can be readily simplified to classical forms when particle geometry is chosen. Do (1998) presented the solution for spherical particle, and in Equation (24), generic solutions for the three traditional particle shapes are presented, with γ_n the roots of characteristic equations presented in Table 4.

$$F = 1 - \sum_{n=1}^{\infty} \frac{2(S+1)(1+\xi)Bi^2}{\gamma_n^4 + \gamma_n^2 Bi[Bi - 2\xi(S+1) - (S-1)] + Bi^2\xi(1+\xi)(S+1)^2} \exp(-\gamma_n^2\tau) \tag{24}$$

Table 3 Characteristic equations for computation of finite bath solutions with negligible external resistance to mass transfer (Crank 1975)

Shape	Characteristic equation
Plane	$\xi\tan(\gamma_n) = -\gamma_n$
Cylinder	$\gamma_n J_0(\gamma_n) = -2\xi J_1(\gamma_n)$
Sphere	$(3\xi + \gamma_n^2)\tan(\gamma_n) = 3\xi\gamma_n$

Table 4 Characteristic equations for computation of finite bath solutions with external resistance to mass transfer

| Shape	Characteristic equation
Plane	$(\gamma_n^2 - \xi Bi)\tan(\gamma_n) = \gamma_n Bi$
Cylinder	$(\gamma_n^2 - 2\xi Bi)J_1(\gamma_n) = \gamma_n Bi J_0(\gamma_n)$
Sphere	$(\gamma_n^2 - 3\xi Bi)[1 - \gamma_n \cot(\gamma_n)] = \gamma_n^2 Bi$

Equation (24) is the same for PVSDM, PVDM and SDM (or HSDM), since it was considered a linear adsorption equilibrium relationship, that is, the Henry Law. This equation will be continuously considered in this paper to evaluate some model simplification, and it will be called as finite bath diffusion model, FBDM.

As it happens with solution presented in Equation (16) for infinite bath, the solutions presented in Equations (23) and (24) converge rapidly when dimensionless time τ is high, and then, only the first term of the sum is sufficient to provide reasonable values (Lyn 1996).

It is important to notice that in adsorption systems involving adsorption in well-agitated baths, intraparticle diffusional resistance is usually the step that controls the adsorption rate; that is, the Biot number usually tends to infinite. It is worthwhile to analyse the lower Biot number value that one can assume a value high enough to neglect the external resistance to mass transfer. Figure 1 presents contour lines comparing the deviations between Equation (23) and Equation (24), that is, neglecting and considering external resistance to mass transfer. In Fig. 1, this comparison can be seen, considering spherical particles and with mass capacity factor ξ equal to 1 (graphical comparison for other geometries and ξ are presented in the Supplementary Material). Considering a percentual deviation of 1% as the minimum required accuracy, at Biot number equal to 1000, neglecting the external resistance to mass transfer is only suitable when fractional uptake is higher than 0.4. For lower values of Biot number, even higher fractional uptakes are needed. It is important to observe that at such high Biot number, the fractional uptake increases extremely rapid at the beginning of the process. Furthermore, it is in accordance with Fig. 1B,

where relatively low values of Biot number can lead to a good accuracy if the dimensionless time is not so close to zero. For instance, considering a τ equal to 0.2, an accuracy of 1% is obtained with a Biot number around 15, a considerably small value that already allows one to neglect external resistance to mass transfer.

In Fig. 2, it is presented the fractional uptake computed as a function of dimensionless time τ for different values of mass capacity factor ξ, for spherical particles and Bi equal to 1. It was used Equation (16) when ξ is equal to 0, since it defines an infinite bath, and Equation (24) for values of ξ higher than zero. It is important to notice that the typical values of ξ usually are in the range from 0.1 to 10 that, for a linear adsorption isotherm, lead to percentual removal from 0.91 to 0.09. It becomes clear that the infinite bath predictions (black line in Fig. 1) are quite different than the usual behaviour. Although one could suppose that when its measured values of adsorbed concentration, q, are normalized with the equilibrium values q_e, leading to calculation of the fractional uptake according to Equation (12), it becomes clear from Fig. 2 that this normalization does not lead to similar prediction. Furthermore, when researchers consider
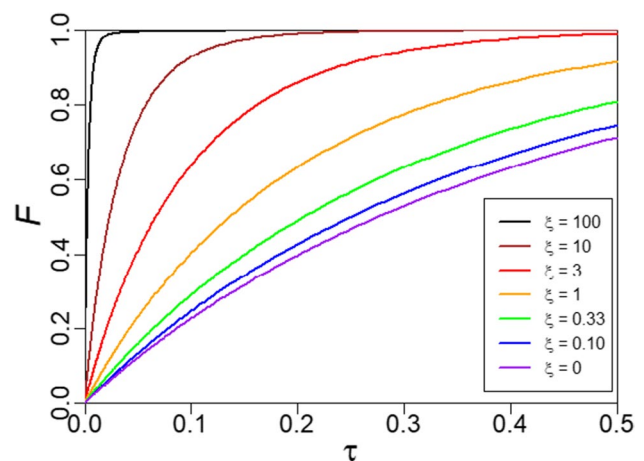
Fig. 2 Fractional uptake computed for finite bath with different values of mass capacity factor ξ and for infinite bath ($\xi = 0$), with $Bi = 1$ and spherical particles

Fig. 1 Contour lines of percentual deviations between predictions neglecting (Equation (23)) and considering (Equation (24)) external resistance to mass transfer for spherical particles and ξ equal to 1
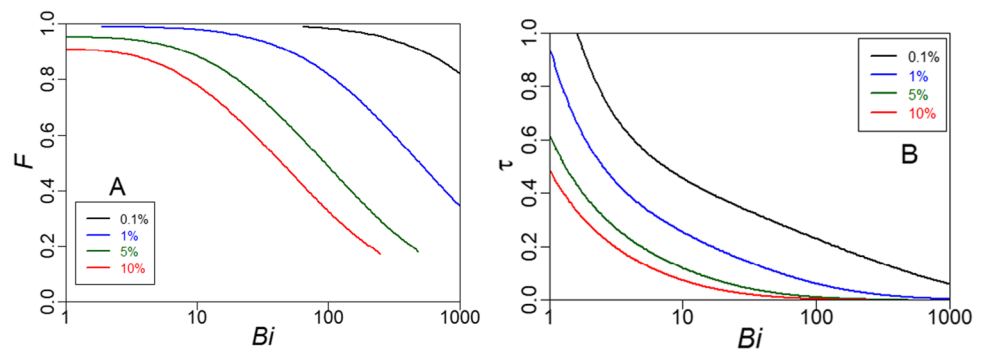
equations derived from an infinite bath approach to estimate the mass transfer parameters, they should be aware of the estimation of biased values, since the parameter values will be dislocated to compensate for different model predictions.

Consequently, these solutions considering the change in the bulk concentration over time can lead to predictions that are much closer to the usual experimental conditions when compared with prediction obtained with models based the infinite bath approach. Despite this, analytical solutions for finite bath systems with a linear adsorption isotherm are rarely considered (Edeskuty and Amundson 1952; Dotto and Pinto 2012; Brandani 2020).

EMT model

Until now, the mass transfer-based models presented in this paper always considered internal resistance to mass transfer, that is usually the common case, since rate of diffusion inside the particle pores tends to be the rate-limiting step. However, when particle characteristic length is small and the bulk phase is not vigorously agitated, one may find conditions where only external mass transfer is significant and concentrations inside particle do not vary significantly along the space. In this case, two ordinary differential equations describing the mass balance in the bulk phase and the mass balance in the solid phase, respectively, Equations (25) and (26), are sufficient to describe the entire system. (A detailed derivation of these equations is presented in Section S1 of the Supplementary Material.)

$$\frac{dC_b}{dt} = -\frac{M}{\rho_p V}\frac{(S+1)}{R}k_m(C_b - C_p) \tag{25}$$

$$\frac{dC_p}{dt} = \frac{1}{(\varepsilon + \rho_p K)}\frac{(S+1)}{R}k_m(C_b - C_p) \tag{26}$$

Initial conditions are still necessary. At the beginning, bulk concentration is equal to C_{B0}, and adsorbed concentration q is usually equal to zero, since usually a fresh adsorbent is used in the experiments. Furthermore, concentration in the adsorbed phase q and concentration at the particle C_P can be assumed at equilibrium and are related to each other through the adsorption isotherm, as shown in Equation (2). In general, this system of two ordinary differential equations does not have analytical solution because the nonlinearity that was introduced by the equilibrium relation. However, since it is being considered a linear adsorption isotherm, simultaneous solution of Equations (25) and (26) lead to Equations (27) and (28):

$$C_b = \frac{C_{b0}}{(1+\xi)}\{1 + \xi \exp[-(1+\xi)(\frac{S+1}{\varepsilon + \rho_p K})\frac{k_m}{R}\ t]\} \tag{27}$$

$$C_s = \frac{C_{b0}}{(1+\xi)}\{1 - \exp[-(1+\xi)(\frac{S+1}{\varepsilon + \rho_p K})\frac{k_m}{R}\ t]\} \tag{28}$$

From Equation (28), it can be seen that the equilibrium concentration (taking the limit as t goes to infinity) is equal to the term outside the brackets. Then, the fractional uptake can be computed according to.

$$F = 1 - \exp[-(1+\xi)(\frac{S+1}{\varepsilon + \rho_p K})\frac{k_m}{R}\ t] \tag{29}$$

The EMT model is sometimes called the Furusawa and Smith model, since these authors probably were one of the firsts to publish this model (Furusawa and Smith 1973; McKay and McConvey 1981; McKay et al. 1986).

One question that frequently arises is the definition of the critical value of Biot number that defines the validity of EMT model. On straightforward way to evaluate this is a comparison between prediction with EMT model and the FBDM, presented in Equation (24), that consider both intraparticle and external resistance to mass transfer. For this, Equation (29) is rewritten according to Equation (30), where fractional uptake is written as a function of Biot number and dimensionless time τ.

$$F = 1 - \exp[-(1+\xi)(S+1)Bi\ \tau] \tag{30}$$

In Fig. 3, these model predictions are compared for spherical particles, S equal to 2, and with a mass capacity factor ξ equal to 1. It is important to notice that this comparison considers that adsorption equilibrium follows a linear relationship, that is, follows Henry Law, since this assumption was done in the development of Equations (24) and (30).

Observing Fig. 3A, where the percentual deviations of EMT model with respect to Equation (24) are presented, it can be seen that with a Biot number lower than 0.1, the percentual deviation of EMT model is lower than 1%. In Fig. 3B, a similar trend is observed, but it also can be seen that when that even when Biot number is high, that is $Bi > 10$, if dimensionless time τ are higher than 0.3, EMT model becomes suitable. This happens because fractional uptake is close to 1 for EMT model and FBDM, and both model predictions are similar.

Additional evaluation of EMT model (see the Supplementary Material) for the three traditional geometries showed that slightly lower values of Biot number are necessary to achieve the same accuracy for cylindrical particles and even slightly lower for slab particles. It also evaluated different values of the mass capacity factor ξ, and it was found that the value of ξ has a marginal effect on the contour levels: An increase of the value of ξ leads to a slight increase in the EMT accuracy. However, it is important to observe that the effects of particle geometry and ξ value are small and the critical value of Biot equal

Fig. 3 Contour lines of percentual deviations of EMT model with respect to FBDM (Equation (24)) for spherical particles and ξ equal to 1
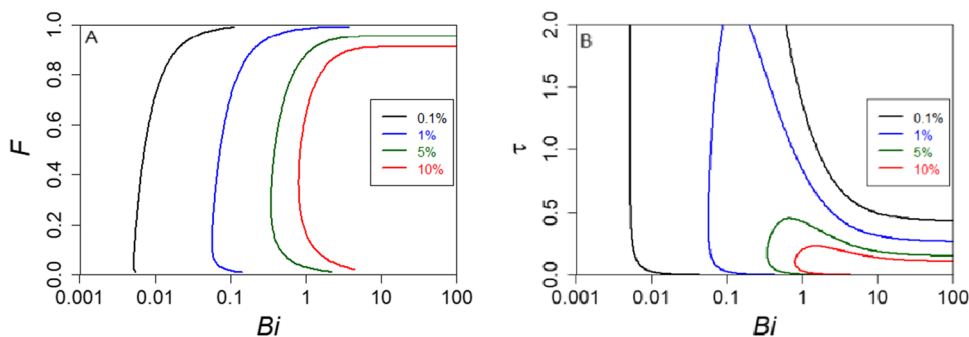
0.1 is a good value to compute values with an accuracy (percentual deviation) around 1%. One can argue that experimental measurements are usually not obtained with such accuracy, and it is not imperative for the model to be so accurate; in this case, one can find appropriate the use of EMT model even with when Biot number is equal 1. Do and Rice (1990) stated that EMT model can be considered valid when Biot number is lower than 0.2, although they did not define the level of deviation with this Biot value. By the other side, if someone is interested in more accurate predictions, EMT model should be considered only for even lower values of Biot number.

LDF model

The linear driving force model was suggested by Coates and Glueckauf (1947) and Glueckauf (1955) in order to describe intraparticle mass transfer in adsorption processes in a simplified form. Rather than considering the partial differential equation presented in Equation (3), LDF model simply defines that the rate of adsorption is proportional to the difference between an hypothetical adsorbed concentration q^* that would be at equilibrium with bulk concentration C_B and the current average adsorbed concentration $\overline{q}$, according to the Equation (31), where k_{LDF} is the proportionality constant that can be related to the homogeneous particle diffusivity, D_h, and particle size for spherical particles as shown in Equation (32) (Glueckauf 1955; Li and Yang 1999; Rodrigues and Silva 2016).

$$\frac{d\overline{q}}{dt} = k_{LDF}(q^* - \overline{q}) \tag{31}$$

$$k_{LDF} = \frac{15D_h}{R^2} \tag{32}$$

A generic version of Equation (32) can be obtained for other tradition particle geometries (different values of S) and also considering a generalized concentration profile (Liaw

et al. 1979; Li and Yang 1999; Sircar and Hufton 2000a; Patton et al. 2004). Considering a parabolic concentration profile, Equation (33) is obtained. (Development of this equation is shown in the Supplementary Material.)

$$k_{LDF} = \frac{(S + 1)(S + 3)D_{app}}{R^2} \tag{33}$$

The change in the bulk concentration can be defined according to the Equation (34):

$$\frac{dC_B}{dt} = -\frac{M}{V}k_{LDF}(q^* - \overline{q}) \tag{34}$$

Considering a linear adsorption isotherm, Equations (31) and (34) can be solved leading to an analytical solution, as shown in Equation (35). Factional uptake can again be readily computed according to the Equation (36):

$$q = \frac{C_{b0}K}{1 + \xi}\{1 - \exp[-(1 + \xi)k_{LDF}\,t]\} \tag{35}$$

$$F = 1 - \exp[-(1 + \xi)k_{LDF}\,t] \tag{36}$$

It is important to observe the similarities between Equations (29) and (36) for computation of the fractional uptake, respectively, with the EMT and LDF models applied to batch adsorption process. The mathematical behaviour of both equations is similar; the difference is only related to the value of constant k_{LDF} and the value of the group $(S + 1)k_m/(R\rho_p K)$. Consequently, when these models are used to describe experimental data from batch adsorption experiments and the values of parameters k_{LDF} and k_m are estimated, the quality of both model fits will be the same, not allowing the discrimination between these two models, although being based on different theoretical approaches.

In order to compare LDF model with FBDM based on Equation (24), Equation (33) was used in Equation (36), leading to Equation (37), allowing fractional uptake predicted by LDF model to be plotted as a function of dimensionless time τ, as shown in Fig. 4.
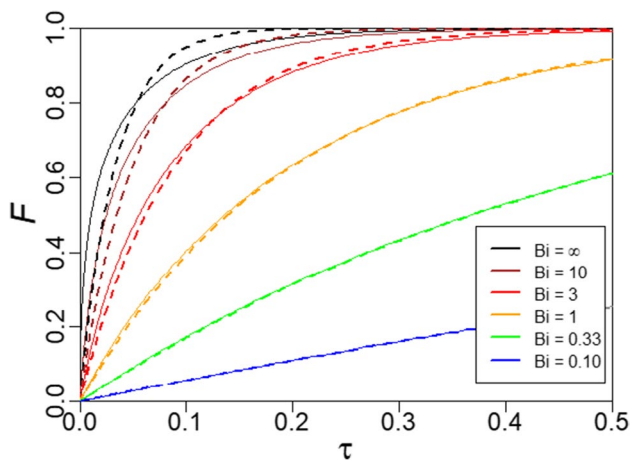
Fig. 4 Fractional uptake computed with LDF model (dashed lines) and FBDM (full lines) considering external resistance to mass transfer with, ξ equal to 1 and for spherical particles

$$F = 1 - \exp[-(1 + \xi)(S + 1)(S + 3)\,\tau] \qquad (37)$$

However, Equation (37) is valid only when external resistance to mass transfer is negligible, that is, when Biot number tends to infinity. Considering Equation (25) for description of bulk phase concentration variation, Equation (31) for adsorbed concentration and Equations (9) and (10) as a boundary condition between these two phases, a solution can be derived leading to a LDF model that take into account external resistance to mass transfer, as shown in Equation (38) (Rice 1982; Hills 1986):

$$q = \frac{C_{b0}K}{1 + \xi}\{1 - \exp[-(1 + \xi)(\frac{Bi}{(S + 3) + Bi})k_{LDF}\,t]\} \qquad (38)$$

In order to compare this LDF model with finite Biot values, Equation (38) is rewritten according to Equation (39), where Equation (33) is also considered to allow the computation of the fractional uptake as a function of the dimensionless time. Then, predictions with this model were compared with FBDM in order to evaluate the applicability of LDF model, as shown in Fig. 4.

$$F = 1 - \exp[-(1 + \xi)(S + 1)(S + 3)(\frac{Bi}{(S + 3) + Bi})\,\tau] \qquad (39)$$

It can be seen in Fig. 4 that LDF model prediction are close to predictions from FBDM when Biot number is lower than 1. It is expected since at low Biot values, external resistance is the rate controlling step and these two models (and EMT model) lead to similar results. However, at high Biot values, LDF model is not able to predict values close to FBDM. Some works (Glueckauf 1955; Yang 1997) stated that LDF model is valid only when dimensionless time τ is higher than 0.1, since at the beginning of the adsorption batch process, the quadratic approximation for the concentration profile inside adsorbent particle is not adequate. However, when Biot number is high, the fractional uptake increases very quickly, as shown in Fig. 4.

In order to allow a better evaluation, percentual deviations between LDF and FBD model were computed for several values of dimensionless time, fractional uptake and Biot number, and the contour lines of the percentual deviation are shown in Fig. 5 (figures for different values of ξ and different particle geometries can be found in the Supplementary Material). It is reasonable to define that LDF model is suitable when dimensionless time is higher than 0.1 (Fig. 5B). However, considering Fig. 5A, if a maximum percentual deviation of 1% is considered, LDF model is not suitable when Biot is higher than 5 (in fact, it will be suitable only in a narrow range around a fractional uptake of 0.8 and when this value is close to 1). However, if one considers 5% as the maximum allowable percentual deviation, that LDF model can be considered suitable when fractional uptake is higher than 0.76 (this is the value for conditions considered to draw Fig. 5; although this value is different for other conditions, the overall conclusions are similar, according to figures presented in the Supplementary Material).

It also can be seen in Fig. 5 that LDF model is suitable for low values of Biot number. However, this happens because it was considered a LDF model with external resistance to mass transfer. It seems that LDF model is suitable at critical Bi values slightly higher than EMT model (see Fig. 3). It is important to observe that when adsorption on heterogeneous

Fig. 5 Contour lines of percentual deviations of LDF model with respect to FBDM (Equation (24)) for spherical particles and ξ equal to 1
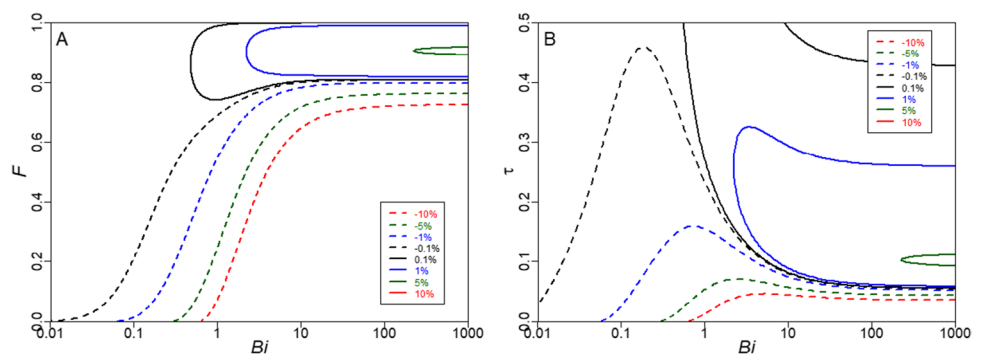
solids is considered, LDF model usually works for description of adsorption kinetics because the details of the adsorption kinetics are lost particularly in the evaluation of overall uptake (Sircar and Hufton 2000b). However, one should be aware when using LDF model in the estimation of diffusivities, since it can be obtained biased values due to model differences from more rigorous models that considers a more accurate concentration profile inside adsorbent particle (Hills 1986; Do and Rice 1990).

Further simplified models

In this section, it presented two simplified models usually considered to describe kinetic data from batch adsorption experiments. Both models are based on analytical solutions obtained for infinite bath without external resistance to mass transfer and considering a linear isotherm to describe the equilibrium of adsorption.

Time square root model

The solutions presented in Table 2 can be simplified considering only the term where dimensionless time is raised to 1/2; that is, the fractional uptake (or the adsorbed concentration q) is considered proportional to the square root of time, according to the Equation (40):

$$F = 2(S+1)\sqrt{\frac{\tau}{\pi}} = 2(S+1)\sqrt{\frac{D_{app}}{\pi R^2}}\sqrt{t} \qquad (40)$$

This simplification is only reasonable if some conditions are observed. The principal restriction is that this simplification is reasonable only when applied to the beginning of the batch adsorption processes and it is so because of three reasons: Firstly, the solutions presented in Table 2 were developed considering that bulk concentration remains constant over time, that is, an infinite bath; secondly, it was considered a linear adsorption isotherm that is also suitable at the beginning when concentrations

inside adsorbent particles are still at a low level; thirdly, considering only the term with the square root of time is only reasonable at low values of time, since the other terms can be neglected. These three conditions are reasonable satisfied at the beginning of the batch adsorption process. However, it is important to clearly state the duration of this initial part of the process when the square root model is adequate.

In Fig. 6, the difference between fractional uptake form square root model and infinite bath model are presented as a function of fractional uptake and dimensionless time. For plane adsorbent particle ($S=0$), the square root model can provide reasonable prediction (deviation lower that 0.01) for fractional uptake up to 0.7. However, when cylindrical ($S=1$) and spherical ($S=2$) particles are considered, reasonable predictions are obtained only for fractional uptakes lower than 0.2. Figure 6B also shows that for these particle geometries, reasonable predictions are only obtained at very low dimensionless time values. It can be observed in Table 2 that for cylindrical and spherical particles, a linear term of τ must be discarded to obtain the square root model. For plane particles, only the sum of integrals of complementary error function are discarded, and these values are only relevant at high time values. For this reason, the square root model works better for plane particles and does not seem a good choice when working with cylindrical or spherical particles.

Although this clear limitation on its prediction quality, the square root model is routinely used to evaluate intraparticle diffusion, and it is commonly called as "Weber and Morris intraparticle diffusion model" (Weber and Morris 1963). Usually, this model is represented by Equation (41), where the adsorbed concentration q varies linearly as a function of the square root of time, where K_{id} is defined as the intraparticle diffusion rate constant (in fact, K_{id} is a lumped parameter (Simonin and Bouté 2016), as can be seen through comparison between Equations (40) and (41)), and C is a constant that is usually erroneously related to the thickness of the boundary layer (Ahmad and Rahman 2011; Chen and Zhang 2014; Vinhal et al. 2015; Basu et al. 2018).

Fig. 6 Comparison between square root and infinite bath models (dashed lines indicate where difference between model predictions is 0.01 and 0.05)
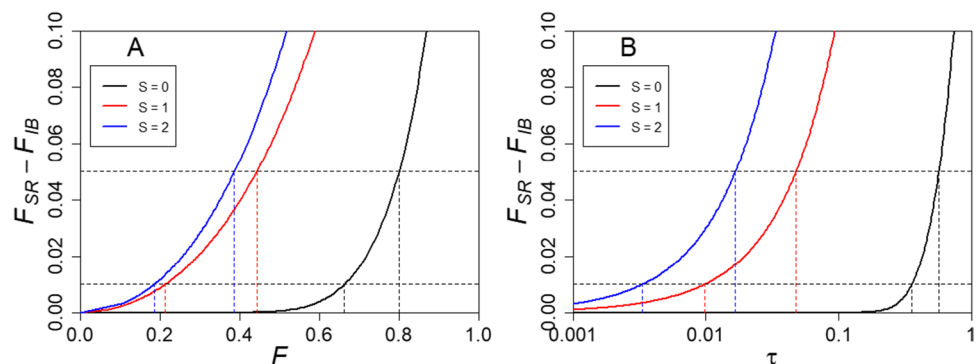
$$q = K_{id}\sqrt{t} + C \tag{41}$$

It is important to notice that solutions presented in Table 2 were obtained for the case when external resistance to mass transfer can be neglected. If the experimental data follows this assumption, the line plot of q versus square root of time will pass through the origin. If there is significant external resistance to mass transfer, the line will not pass through the origin. Unfortunately, there are too many papers published in the literature that erroneously compute a positive value of constant C and ascribe it to the thickness of the boundary layer (Srivastava et al. 2006; Ahmad and Rahman 2011; Basu et al. 2018). However, when an additional resistance is considered, it seems reasonable that it must have a negative effect on the rate of adsorption, leading to a negative value of C. This was clearly shown in a previous paper (Schwaab et al. 2017), when solutions for semi-infinity slabs with and without external resistance to mass transfer were compared, showing that when external resistance to mass transfer is significant, the constant C must be negative. Positive values of constant C have been found in the literature probably because experimental values measured at high time values are being used, that is, experimental conditions where time square root model is not more suitable to describe the batch adsorption behaviour.

Another common mistake when considering this model is to represent the data as a sequence of linear sections and assigning a specific mass transfer mechanism to each one (Allen et al. 1989; Ho and McKay 1998; Koumanova et al. 2003; Alkan et al. 2007). There are some works (Malash and El-Khaiary 2010; El-Khaiary and Malash 2011) that even proposed the use of a piecewise linear regression tool to clearly identify each one of the linear segments. However, the use of this sequence of linear sections does not have any rigorous physical foundation and should not be used to analyse kinetic data from batch adsorption experiments (Chatterjee and Schiewer 2014; Da Ros et al. 2017; Inglezakis et al. 2019).

For these reasons, the linear relationship between adsorbed concentration (or fractional uptake) with square root of time must be carefully considered and, in our opinion, should not be used to describe kinetic data, since it is based in an approximation of model that considers an infinite bath that already is a rough approximation of actual condition considered in batch adsorption experiments.

Boyd-Reichenberg model

Another model based on mass transfer that is frequently considered is the Boyd model (Boyd et al. 1947). However, in this work, Boyd and co-workers considered the model presented in Equation (16) for spherical particles with characteristic values computed according Table 1, as

shown in Equation (42). It is important to keep in mind that this solution is only valid for an infinite bath, where adsorption equilibrium follows a linear isotherm and without external resistance to mass transfer.

$$F = 1 - 6\sum_{n=1}^{\infty} \frac{1}{(n\pi)^2}\exp(-\frac{(n\pi)^2 D_{app}t}{R^2}) \tag{42}$$

However, the model usually called as Boyd model was indeed proposed by Reichenberg (1953) that considered a model that combines Equation (42) with only the first term in the summation with the solution presented in Table 2 for spherical particles, taking into account the square root and linear terms, as shown in Equation (43). In fact, (Boyd et al. 1947) considered only the term with the square root of time for the initial period. This simplified model based on solution found through Laplace transform method is suitable for low time values, that is, $\tau < \tau_{crit}$. By the other side, considering only the first term of summation in Equation (42) is suitable for high time values, that is, $\tau \geq \tau_{crit}$. Consequently, it seems reasonable that combining these two models, a simplified model with reasonable prediction quality can be obtained.

$$F = \begin{cases} \frac{6}{\sqrt{\pi}}\sqrt{\tau} - 3\tau & \tau < \tau_{crit} \\ 1 - \frac{6}{\pi^2}\exp(-\pi^2\tau) & \tau \geq \tau_{crit} \end{cases} \tag{43}$$

In fact, Boys model is usually presented according Equation (44), where B is a parameter defined in Equation (45):

$$F = \begin{cases} \frac{6}{\pi^{3/2}}\sqrt{B\,t} - \frac{3}{\pi^2}B\,t & t < t_{crit} \\ 1 - \frac{6}{\pi^2}\exp(-B\,t) & t \geq t_{crit} \end{cases} \tag{44}$$

$$B = \frac{\pi^2 D_{app}}{R^2} \tag{45}$$

In Fig. 7, the Boyd-Reichenberg model presented in Equation (43) is compared with solution for infinite bath, presented in Equation (16) (Equation for sphere from Table 2 could also be considered).

In this figure, the dashed lines indicate the values of τ_{crit} and F_{crit} that are approximately equal to 0.1575 and 0.875. At this point, the deviation of the fractional uptake computed from Boyd-Reichenberg model from the value computed with complete solution of infinite bath is the highest value and is only 0.0003; that is, Boyd-Reichenberg model is a very good option to simplify the complete solution. The Boyd-Reichenberg model was presented only for spherical particles, although solutions for plane and cylindrical
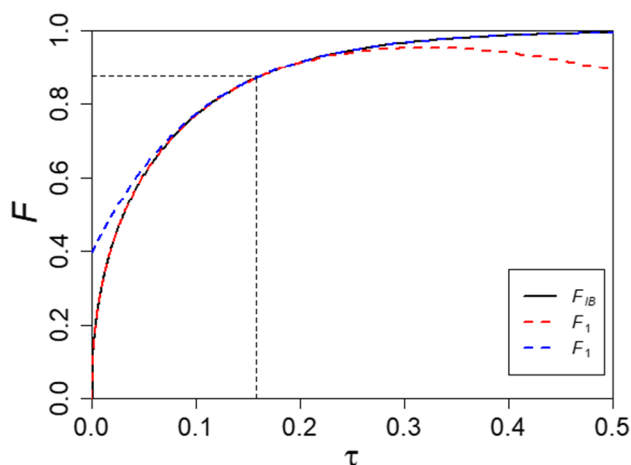
Fig. 7 Comparison between Boyd-Reichenberg model (red and blue dashed lines) and infinite bath model (black line)

Table 5 Summary of the model assumptions (all these models considered a linear adsorption isotherm)

Model	Equation	External resistance?	Internal resistance	Variable bulk concentration?
FBDM	Eq.(24)	Yes	Yes	Yes
	Eq.(23)	No	Yes	Yes
IBDM	Eq.(14)	Yes	Yes	No
	Eq.(16)	No	Yes	No
EMT	Eq.(30)	Yes	No	Yes
LDF	Eq.(39)	Yes	Yes*	Yes
	Eq.(37)	No	Yes*	Yes
TSR	Eq.(40)	No	Yes	No
BR	Eq.(43)	No	Yes	No

*Internal resistance is considered in simplified form

particles can be readily obtained (see the Supplementary Material).

It must be pointed out that, although Boyd-Reichenberg model is able to reproduce almost perfectly the prediction from infinite bath model, these both models are based in the assumption that bulk concentration does not change over time. There are some mass transfer problems where this assumption is valid (Perez et al. 2011; Mercali et al. 2021). However, the commonly conditions considered in the study of kinetic batch adsorption are not in agreement with this assumption, since it is the decrease in the bulk concentration that is used to analyse the kinetics of batch adsorption experiments. Furthermore, Boyd-Reichenberg and infinite bath models also assume that there is no significant external resistance to mass transfer (that is usually a good assumption) and that adsorption equilibrium can be described by a linear isotherm (that is reasonable only in the beginning of the process when the true adsorption isotherm is nonlinear).

Consequently, one should be aware when considering Boyd-Reichenberg model and square root model to evaluate mass transfer parameter, that is, intraparticle diffusion coefficients, since even if model predictions are close to experimental data, the estimated parameter values are likely to be biased.

Final considerations

The mathematical models presented in the previous sections are based on mass transfer phenomena and are described by partial differential equations whose analytical solutions are possible only when equilibrium of adsorption can be described by a linear equation, that is, the Henry Law. When adsorption equilibrium must be described by a nonlinear equation, numerical methods can be promptly employed to solve the mass transfer-based models. However, even though numerical methods are available in many different computational languages and software, most of published papers still consider simplified models that are based on inaccurate assumptions.

In Table 5, a summary of assumptions considered in the development of each model are presented. One assumption that is usually satisfied is the negligible external resistance to mass transfer. It happens because the baths used for kinetic adsorption experiments are usually very well mixed and, consequently, intraparticle mass diffusion is the only rate limiting step. It is important to notice that this fact does not invalidate the models that consider external resistance, since these models will reproduce the behaviour of models that neglect external resistance to mass transfer when Biot number is set at high values, as shown in Fig. 1.

In this way, the external mass transfer model is very unlikely to provide a detailed description of experimental kinetic data. Even if this model could be able to describe a single experiment, its use to predict batch adsorption performance at different conditions will be probably meaningless.

Similarly, the linear driving force model, that is based on simplifications of the intraparticle diffusion models, consists in an equation that are mathematically equivalent to the external mass transfer model, and should not be considered suitable for a detailed description of batch adsorption processes.

But without any doubt, the weakest hypothesis is the assumption that bulk concentration does not vary during the batch adsorption experiment. Time square root and Boyd-Reichenberg models are solutions based on this hypothesis, also known as infinite bath assumption. Considering constant bulk concentration, from an optimistic point of view, would be a reasonable assumption for the data just at the beginning of the experiment since it could be assumed that bulk concentration has not varied significantly. But the

extent of this initial stage is usually very short, since the decrease in the bulk concentration is very fast in the initial adsorption period. For this reason, one must be very careful in considering these simplified models; in fact, these models should not be considered for description of batch adsorption processes.

An interesting option is the analytical solution for finite bath diffusion model, FBDM, although it is rarely considered. The only weakness of this solution is considering a linear isotherm (Henry Law). However, when adsorption is considered for removal of low concentration pollutants, FBDM model can be promptly considered, since in this case it can be expected that a linear isotherm will provide a good description of the adsorption equilibrium.

Finally, one could argue that even using these simplified models, it is possible to predict the behaviour of batch adsorption kinetics. And it really can be true, because the shape of all curves predicted by the models presented previously are very close. Then, when just one kinetic curve is considered, almost any model can describe this data by adjusting the values of some parameters, like mass transfers constants or even adsorption equilibrium constants. However, if someone uses this model, with parameters fitted to one specific batch adsorption experiment, to predict the behaviour at different experimental conditions, probably the quality of prediction will be very poor. It can be expected that rigorous models, like FBDM, will provide a reasonable prediction even when experimental conditions are modified. For this reason, it is very important that batch adsorption experiments were carried out at different experimental conditions such as initial concentration, solution volume to adsorbent mass ratio and, if possible, different particle adsorbent sizes. Then the mathematical model that is being considered must be able to describe all kinetic curves with the same estimated parameters. Furthermore, a good strategy to evaluate a model is letting some of the experimental kinetic curves out of the parameter estimation step and using these data later to observe if the model can predict these experimental data that was not considered in the parameter estimation step, providing a validation test to the model. Although it seems a hard and laborious procedure, this will provide an actual evaluation of the mathematical models considered to describe the batch adsorption data, and this model with its estimated parameters can be used with more confidence for optimization, design and any other purposes.

Conclusions

In this critical review, some simplified models were analysed, and the assumptions considered in their development were highlighted. Although negligible external resistance to mass transfer is usually a reliable assumption, infinite bath consideration is completely inaccurate, since it is just the decrease in the bulk concentration that is usually measured to determine the kinetic of batch adsorption process. Another common assumption is the Henry Law (linear adsorption isotherm); although it is not a widely correct assumption, it is valid when one works with solution at low concentration levels.

It must be emphasized that nowadays numerical procedures are widely available and rigorous solution for finite bath adsorption, with or without external resistance to mass transfer, can be obtained when a nonlinear isotherm is considered. Consequently, the analysis of kinetic adsorption data from batch experiments is much more reliable and permits to researchers a deeper understanding of the kinetic adsorption mechanism that also allow model improvement and are very useful for development of adsorption processes.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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