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Implications of Apparent Pseudo-Second-Order Adsorption Kinetics onto Cellulosic Materials: A Review

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The pseudo-second-order (PSO) kinetic model has become among the most popular ways to fit rate data for adsorption of metal ions, dyes, and other compounds from aqueous solution onto cellulose-based materials. This review first considers published evidence regarding the validity of the mechanistic assumptions underlying application of the PSO model to adsorption kinetics. A literal interpretation of the model requires an assumption that different adsorption sites on a solid substrate randomly collide with each other during a rate-limiting mechanistic step. Because of problems revealed by the literature regarding the usual assumptions associated with the PSO model, this review also considers how else to account for good fits of adsorption data to the PSO model. Studies have shown that adsorption behavior that fits the PSO model well often can be explained by diffusion-based mechanisms. Hypothetical data generated using the assumption of pseudo-first-order rate behavior has been shown to fit the PSO model very well. In light of published evidence, adsorption kinetics of cellulosic materials is expected to mainly depend on diffusion-limited processes, as affected by heterogeneous distributions of pore sizes and continual partitioning of solute species between a dissolved state and a fixed state of adsorption.

Keywords: Kinetics of adsorption; Cellulose; Wood-based materials; Mesoporous substrates

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INTRODUCTION

Importance of Adsorption

Adsorbent materials, including activated carbons, zeolites, and cellulose-based materials, hold great promise as means to remove various dissolved compounds or metal ions from aqueous solution. Researchers have pursued the development of lower-cost sorbent materials and evaluated them for removal of a wide variety of pollutants. At the same time, there has been much attention to both the rates and the capacities of adsorption. Table 1 lists some review articles that cover various aspects of this topic.

Table 1. Reviews of Research Using Adsorbents to Remove Pollutants from Aqueous Systems

Substances to be removed	Classes of adsorbents	Reference
Metal ions	Agro-based biomass	Demirbas 2008
Metal ions	Cellulose-based	Hubbe *et al.* 2011
Dyes	Agro-based biomass	Salleh *et al.* 2011
Dyes	Cellulose-based	Hubbe *et al.* 2012a
Dissolved petrochemicals	Cellulose-based	Hubbe *et al.* 2014
Dyes	Various adsorbents	Yagub *et al.* 2014

Quantification of adsorption rate information generally requires the use of suitable model equations. Here the word “model” is often assumed to mean that the equations employed represent theoretically justifiable mechanisms that can – at least as an approximation – account for the observed adsorption data in a theoretical sense. Whether or not the equations are grounded in a meaningful theory, a mathematical fit of such data also could be employed when estimating the dimensions or process conditions in a planned wastewater treatment facility.

The rates of uptake of target compounds onto the adsorbent are of great importance with regards to potential scale-up and implementation of prospective systems to remove pollutants from water. If the time required for effective adsorption can be shortened, then it may be possible to decrease the retention time in a batch system or packed bed system. The size of the needed equipment might be less. Packed bed systems are often regarded as being more practical, since they avoid the need to collect suspended particles again by filtration, settling, or other means after their usage (Schweich and Sardin 1981; Ali 2014). Within a packed bed or column, each packet of fluid does not have time to fully equilibrate with adjacent particles of adsorbent as it passes through the system. Accordingly, there is an understood preference of adsorbent systems that can act fast (Sen Gupta and Bhattacharyya 2011; Largitte and Pasquier 2016).

The kinetics of adsorption also can be important for industrial processes in which compounds are being applied to solids materials from solution. Textile manufactures require a high efficiency and rate of uptake of dyes onto the fibers (Ujhelyiova *et al.* 2007; Varadarajan and Venkatachalam 2016). In papermaking, dyes and various other additives need to be retained in nearly quantitative manner to the surface of cellulosic fibers (Hubbe *et al.* 2008). In agricultural systems there is a need, in many cases, to retain nutrients or pesticides efficiently within soil after their application as solutions (Bailey and White 1964; Calvet *et al.* 1980a,b). Even in the case of conventional wastewater treatment, the rates of adsorption of compounds of pollutant onto sludge particles or other sorbents can impact the quality of the discharged treated water (Gupta and Suhas 2009; Inyang *et al.* 2016).

Importance of the Pseudo-Second-Order Kinetic Model

The focus of this article is on one of the most popular approaches to quantitative description of the rates of uptake of substances onto sorbent materials. Based on a search of the Web of Science, one of the foundational articles describing the usage of a pseudo-second-order (PSO) model to quantify adsorption kinetics (Ho and McKay 1999) has been cited about 8000 times. It was reported in 2015 that out of 5000 citations of this work, 4500 of them indicated best fits to the PSO model, compared to alternative models or equations (Douven *et al.* 2015). A more recent theoretical derivation has been cited over 1000 times (Azizian 2004). The statistical agreement between adsorption data and the PSO model has been found to be high in a wide variety of situations (Sobkowski and Czerwiński 1974; Ritchie 1977; Ho and McKay 1999; Liu and Liu 2008; Hubbe *et al.* 2012a; Hubbe 2013; Tan and Hameed 2017).

Physicochemical soundness, reasonableness, and practical usefulness are themes that will be considered in this review article. Theoretical issues related to the PSO approach have been addressed, in particular, by the articles listed in Table 2.

Table 2. Articles Addressing Theoretical Issues Related to the Pseudo-Second-Order Analysis of Adsorption Rates

Issues addressed	Selected references
Initial bulk concentration too low	Azizian 2004; Lin *et al.* 2018
Activation energy requirement for surface reaction steps	Mills *et al.* 1995
Non-independence of surface sites for the rate-limiting step	Hubbe *et al.* 2012a
Mistakes in copying and citation of the PSO equation	Ho 2014
Range of validity; fundamental basis	Douven *et al.* 2015
Usage of PSO equations merely for data fitting	Tan and Hameed 2017
Simultaneous fits to contradictory kinetic models	Plazinski *et al.* 2009

Another issue, when using models to fit data from practical experiments, is the necessity to make simplifying assumptions. It has been said that all theoretical models are incorrect, but some of them are useful (Box 1976). Often it is only by making simplifying assumptions that one can begin to understand our complex world. However, there is a danger when a simplified description is being used outside of its range of validity.

A third aspect that will be considered is the potential usefulness of data fitting as a means to estimate the size and throughput of industrial equipment. Various publications have suggested that such engineering estimates can be useful for the design and optimization of facility designs for treatment of contaminated waters (Weber and Morris 1963; Wu *et al.* 2009a; Tseng *et al.* 2010; Chatterjee and Schiewer 2014; Hill 2014; Douven *et al.* 2015; Tan and Hameed 2017). As will be discussed, the PSO model can be used to accurately represent relationships between time and uptake of solutes from solution in a majority of typical cases.

The Substance of the Pseudo-Second-Order Model

The prefix "pseudo", when applied to chemical kinetics, refers to systems in which one of the influencing factors is held sufficiently constant during an interaction so that it does not need to be included in a mathematical description of the data (Conners 1990; Hill 2014). For instance, in the case of the pseudo-second-order (PSO) relationship, one is making the implicit assumption that any changes in the initial bulk concentration during the experiment are small enough that they do not affect the kinetic relationship (Blanchard *et al.* 1984; Liu and Liu 2008). From another perspective, the word "pseudo" can be taken to imply that a rate law for adsorption is being expressed in terms of an adsorbed amount q (*i.e.* occupied sites of adsorption) rather than in terms of concentration c of the adsorbing species.

The earliest articles to publish mathematical expressions equivalent to the PSO model of adsorption were apparently those of Sobkowski and Czerwiński (1974), Ritchie (1977), Blanchard *et al.* (1984), and Ho and McKay (1998a,b,c). A related mathematical relationship can be obtained also from earlier work of Coleman *et al.* (1956), who proposed equilibrium expressions for the formation of complexes between divalent copper and pairs of adsorption sites at the surface of peat.

Differential equation for PSO and its meaning

The differential equation proposed by Blanchard *et al.* (1984) can be written in generalized form as (Tan and Hameed 2017):

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{1}$$

In this expression, the term q refers to the amount of adsorbate bound to the substrate at time t, q_e stands for its equilibrium value, and k_2 is the pseudo-second-order rate constant.

Implication concerning rate-limiting step

Based on the structure of Eq. 1, one can draw some conclusions about the steps in the rate-limiting step of a process. The squared term in this equation is an expression of the available sites of adsorption at time t. Because the term is squared, one is in effect assuming that during the rate-limiting step there is a collision between two independent unoccupied sites on the adsorbent material. Thus, according to Coleman *et al.* (1956),

$$2P^- + Cu^{2+} \rightleftharpoons CuP_2 \tag{2}$$

where in the cited work P^- is an anionic site on the adsorbent (peat), and the copper metal ions are divalent. Coleman *et al.* (1956) used this expression only as a means of defining an equilibrium relationship. Blanchard *et al.* (1984) used the same equation as the starting point for deriving Eq. 1, which is the differential form of the PSO relationship.

Integrated forms of the relationship

The integration of Eq. 1 was initially carried out by Blanchard *et al.* (1984), giving the form (with the symbols used by Tan and Hameed 2017),

$$\frac{1}{q_e - q} - \alpha = k_2 t \tag{3}$$

where α is an intercept in a presumed linear relationship. In practice, researchers can plot the experimental values of the term $[1/(q_e - q)]$ against time (t), from which the slope of a line found by linear regression gives the value of k_2.

In addition to Eq. 3, there are other ways to write the integrated form of the relationship (Ho 2006b). These are given (together with the other related expressions) in Table A in the appendix to this article (see Eqs. 3A, 3B, and 3C). In addition, some incorrect forms also have appeared in the literature, as reported by Ho (2016), which presumably resulted from mistakes in copying.

General prediction of a declining rate

Regardless of theoretical considerations, the structure of the PSO relationship, as expressed by Eq. 1, leads to the prediction of a declining rate of uptake. That is because each increment of adsorption causes a corresponding decrease in the difference ($q_e - q$). Because the term ($q_e - q$) is squared, the deceleration of the adsorption rate is amplified. It follows that the PSO relationship, irrespective of any initial meaning, might be used to fit data in which some sites of adsorption take a lot longer to be filled. This is typically the case for diffusion-limited processes whereby adsorption sites far from a pellet's outer surface are more difficult to reach. Another case of strong deceleration of adsorption rate corresponds to a situation where the total number of molecules in the solution matches exactly the surface area of the adsorbent, as discussed by Douven *et al.* (2015). In such situations, adsorption is accompanied by strong depletion of the concentration in the bulk solution.

A related kinetic model: pseudo-first-order

Though the main focus of this review article will be on adsorption data that appear to fit better to a pseudo-second-order (PSO) kinetic model, there will be a need to refer multiple times to a related, and apparently well established kinetic relationship, the pseudo-first-order model. This model has been attributed to Lagergren (1898), and its differential form can be expressed as,

$$\frac{dq}{dt} = k_1(q_e - q) \qquad (4)$$

where the definitions of q_e and q are the same as given earlier following Eq. 1. This relationship follows from an assumption that the rate-limiting step in adsorption depends on collisions between solute molecules or ions with unoccupied single sites at the surface of the adsorbent material. Integration of Eq. 4 yields (Ho and McKay 1998a,b,c; Azizian 2004):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (5)$$

As in the case of the integrated form of the PSO relationship (Eq. 3), it is common practice, based on Eq. 5, to prepare plots of $\ln(q_e - q_t)$ *vs.* t as a means to determine the values of k_1.

SUSPICIOUS ASPECTS OF THE PSO MODEL

The purpose of this section is to discuss certain aspects of the PSO kinetic model that have caused some researchers to call into question its validity or range of applications. For example, Plazinski *et al.* (2009) concluded that the PSO does not correspond to any specific physical situation, but that rather it happens to be able to fit typical adsorption data as an approximation. One of the aspects raising doubt among researchers is an expectation that any "surface reaction" involved in the adsorption would likely take place quickly relative to the time needed for diffusion-dependent processes to be achieved. Another is the expected inability of pairs of unoccupied individual sites on a solid substrate to act as independent entities in any rate-limiting interaction. A third concern relates to the fact that, in almost every study of adsorption from solution, the initial concentration changes significantly, and the expression does not contain a term to account for changes in the bulk concentration. A further concern is related to the unreasonableness of having to assume a significant activation energy associated with typical adsorption steps of ions and other compounds onto typical substrates, especially but not restricted to cases where the participants in the surface interaction have opposite charges. Finally, some reported studies appear to have inconsistencies in the fitting of data to various models.

Expectation that Final Step Ought to Be "Fast"

Figure 1 presents a pictorial impression in which a typical cellulose-based adsorbent material in water is envisioned as a three-dimensional structure with an extensive network of pores having a wide range of diameters and lengths, some portions of which are located relatively deep within the material. Such a view, as in an earlier drawing by Tan and Hameed (2017), would suggest that the time required for diffusion ought to be a sufficient factor to account for kinetic effects. Thus, Tan and Hameed (2017) expressed an expectation that the final act of interaction of the adsorbing species with a surface site would likely take place sufficiently rapidly that it would not serve as a rate-limiting step in the overall interaction. It is commonly understood in the field of chemical kinetics that a reactive step that is relatively rapid is unlikely to be the rate-determining factor in an overall reaction rate (Connors 1990; Denisov *et al.* 2003; Henriksen and Hansen 2008; Rudzinski and Plazinski 2006, 2008; Soustelle 2011; Chatterjee and Schiewer 2014; Douven *et al.* 2015; Ancheyta Juárez 2017; Vallance 2017). Based on these considerations, it seems unreasonable to attribute limitations in overall rates of adsorption to the slowness of collisions of adsorption species with surface sites.

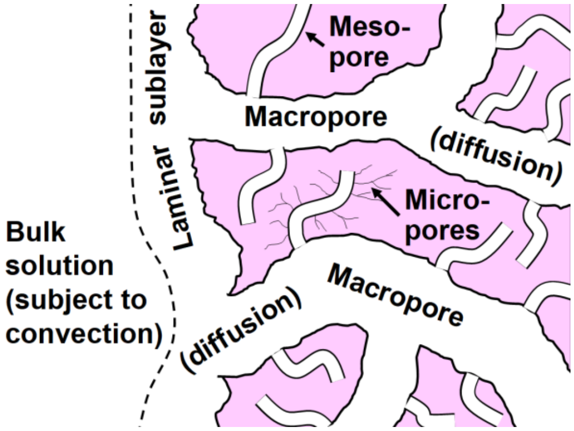

Fig. 1. Representation of a cellulosic material having a three-dimensional porous structure with a range of pore sizes. By IUPAC definition, macropores have diameter greater than 50 nm, mesopores are in the range 2 to 50 nm, and micropores are below 2 nm.

Two factors that also suggest a rapid step in the ultimate attachment of a typical adsorbing species onto cellulose-based materials during a typical adsorption experiment are proximity and molecular simplicity. The word proximity can be understood by envisioning a position in Fig. 1, possibly deep within the cellulosic material within a small pore. The surface area associated with the smallest pores is likely to represent a large proportion of the available adsorption sites, especially in the case of adsorbents such as activated carbons (Perlach 1981; Do and Do 2003; Yahya *et al.* 2015; Suhas *et al.* 2016) and swollen kraft pulp fibers (Stone and Scallan 1968; Alince and van de Ven 1997; Berthold and Salmén 1997; Alince 2002). Within a small pore the adsorbing species are constrained to be very close to a surface. A majority of the studies that have shown good fits to the PSO model have involved relatively small and simple adsorbate species. Since small molecules and ions tend to diffuse rapidly in solution, they would be able to adopt essentially all of their possible molecular conformations within tiny pore spaces in fractions of seconds, including high numbers of collisions with, and possible detachments from, an adjacent solid surface. Relatively long times for a molecule to collide with and adsorb onto a surface, excluding times required for diffusion, have been documented only for quite large molecules, such as high-mass polyelectrolytes (Ödberg *et al.* 1993; Alince 2002; Wu *et al.* 2009b).

Another concern that has been expressed about rate expressions that are based on surface reactions (such as the PSO), is that they do not place needed emphasis on effects related to diffusion (Hubbe *et al.* 2012a; Kumar *et al.* 2017). Mechanisms based on surface reactions as the slow step in adsorption have no way to account for the time needed for diffusion to take place. This concern would be expected to be important in the case of cellulosic materials, given their known complexity of three-dimensional pore structure. If the overall process can be described as shown in Fig. 1, then any model based only on surface reactions could be expected to miss many important factors that influence rates of adsorption. Haerifar and Azizian (2013) presented a new kinetic model that accounts for systems in which both surface reaction and diffusion affect the rate of adsorption at a solid/solution interface.

Impossibility of Mass Action Rule in Case of a Solid

The concept of mass-action, which is a fundamental principle of chemical kinetics, views chemical reactions in terms of collisions among the participating species (Denisov *et al.* 2003; Pekar 2005; Doktorov and Kipriyanov 2007; House 2007; Rudzinski and Plazinski 2008). For example, Boyd *et al.* (1947) mentioned the mass action principles as justification for use of a pseudo-first-order kinetic model. The order of a reaction, as expressed in a rate equation, should be consistent with the numbers of species that need to simultaneously collide during the rate-limiting step (Connors 1990; Denisov *et al.* 2003; Liu and Liu 2008). To take a very simple example, suppose that compound A is reacting with B to form AB, as in

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB} \qquad (6)$$

If one has determined that in fact Eq. 6 represents the rate-limiting step, at a fundamental level, then a rate expression can be written in the form,

$$\mathrm{d[AB]/d}t = k\,\mathrm{[A]\,[B]} \qquad (7)$$

where the terms [A] and [B] are concentrations. Based on Eq. 7 it can be said that the reaction is first-order with respect to both A and B. If, somehow, the concentration of A were held constant during the process, then it would be possible to write an equivalent expression,

$$\mathrm{d[AB]/d}t = k'\,\mathrm{[B]} \qquad (8)$$

in which the modified rate constant *k'* incorporates the concentration of A, which is treated as a constant. Equation 8 can be called a form of "pseudo-first-order" rate expression, since under the conditions of testing, the rate depends only on [B].

Next, one can consider the forward step of a dimerization reaction, as in Eq. 9. In this case, assuming that Eq. 9 represents a rate-limiting step at a fundamental level, the reaction order is two with respect to species A. In other words, the reaction is second-order with respect to [A].

$$A + A \rightarrow A_2 \quad (9)$$

$$d[A_2]/dt = k\,[A]^2 \quad (10)$$

With these examples in mind, the pseudo-second-order relationship, as expressed in Eq. 1 (repeated below) implies some type of collision or interaction between pairs of independent sites of adsorption during the rate-limiting step.

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (1)$$

The problem with the concept just described is that it requires the solid substrate to behave, in terms of the interactions responsible for adsorption, as if it were a liquid. That's essentially what it would mean for pairs of the available sites, represented by the term (q_e – q) in Eq. 1 to be capable if independent action in a proposed second-order rate-limiting process. The situation is illustrated in Fig. 2. Here, in order to model a PSO mechanism with respect to unoccupied surface sites, we assume that an individual adsorbing species in the solution has three possible interactions with an adjacent surface:

(a) It collides with an *occupied* site (result: no sticking).
(b) It collides with a *single unoccupied* site (result: no sticking).
(c) It collides with *two unoccupied* sites at once (result: sticking).

In order to justify a second-order relationship, one has to assume that the sites on the surface are independent of each other. Also one needs to assume that the presence of two unoccupied sites side-by-side is a consequence of random change. Thus, Fig. 2 depicts the unoccupied sites as moving around randomly, *i.e.* surface diffusion of the already-adsorbed species. The topic of surface diffusion will be considered in more depth later in this article. Though the situation represented in Fig. 2 is physically possible, it is suggested here that it does not offer a credible justification for the use of the PSO model to fit typical data for adsorption from solutions.

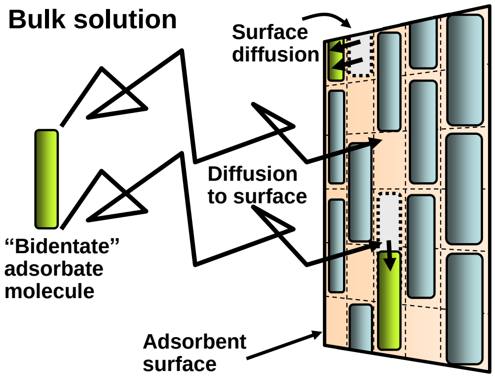

Fig. 2. Schematic illustration to justify use of a PSO mechanism, visualizing unoccupied sites of adsorption moving randomly on the surface and colliding with a frequency proportional to the square of such sites

As an alternative to the surface-adsorption mechanism, one could speculate that some of the available surface sites on an adsorbent material such as peat might be located on separate filaments of cellulosic matter, and that the mutual diffusion of such filaments could possible give rise to collisions between two of the surface sites. Such a concept could be used to rationalize the usage of Eqs. 1 and 3. But realistically, the binding of most materials is expected to involve either individual sites, which might in some cases be composed of two or more functional groups at the surface of an adsorbent. Adjacent functional groups or available locations at a solid surface, being attached to the surface, would not be able to independently collide in a manner that would give rise to the relationship expressed in Eqs. 1 and 3. This problem, when applying Eqs. 1 and 3 to typical adsorption phenomena on solid substrates, was already noted in some earlier publications (Hubbe *et al.* 2012a; Hubbe 2013; Hubbe *et al.* 2014). In particular, a pair of adsorption sites each bound to a solid substrate would act as a single site of adsorption during a realistic rate-limiting step in the process (Hubbe *et al.* 2014). For this reason, the fact that adsorption kinetics often can be well fitted to PSO kinetics may need to be explained starting with different assumptions.

Inconsistency of "Pseudo" Assumption and Experimental Procedures

If one insists upon a strictly accurate analysis, then there is a logical inconsistency inherent in the way that the PSO model is handled in almost every published study where it is used to fit adsorption data. Blanchard *et al.* (1984) introduced the working assumption that the value of bulk concentration would remain sufficiently constant during an experiment such as to allow useful analysis. The term "pseudo" implies that the bulk concentration of adsorbate remains constant during the experiment. However, the results of most adsorption studies are determined based on measured changes in the bulk concentration (Azizian 2004; Hubbe *et al.* 2012a). Thus, the very quantity that is assumed to remain constant is required to change in order to be able to complete the analysis.

Evidence that the problem just described may be important relative to the interpretation of adsorption data comes from studies in which the fitted results were different depending on the initial concentration of adsorbate. A relatively low initial concentration makes it more likely that the overall change in bulk concentration during an adsorption experiment is sufficient to invalidate the working assumption that the concentration remains essentially the same, for purposes of estimation. Strong dependencies of PSO fitting parameters on the initial concentration have been reported in several studies (Ho and McKay 1998a; Azizian 2004; Crini *et al.* 2007; Hameed *et al.* 2007; Tan *et al.* 2008; Lin *et al.* 2018). In the (mostly theoretical) case where diffusion is not a factor limiting the rate of adsorption, Azizian (2004) found that relatively high values of the initial concentration of an adsorbate tend to give good fits to a pseudo-first-order rate behavior, whereas relatively low concentrations often give better fits to a PSO model.

Problems with the Energy of Activation Concept

In cases where a chemical reaction step is truly rate-limiting, it is conventional to explain the slowness of such a reaction step based on an activation energy that is required to reach a defined transition state (Mills *et al.* 1995; Kozuch and Martin 2011). This is illustrated schematically in Fig. 3. Typical reactions that are considered in this way involve the formation of covalent bonds. For example, an activation energy of about 458 kJ/mole is required when the adsorption of H_2 onto copper entails dissociation of the covalent bond (Mills *et al.* 1995).

In principle the scheme shown in Fig. 3 also can be used to explain factors affecting rates of desorption. Thus, the area highlighted by cyan represents the free energy of a hypothetical adsorbed state. The activation energy required to surpass the transition state leading to desorption, in such a situation, would be given by the sum of the two arrows shown in the figure.

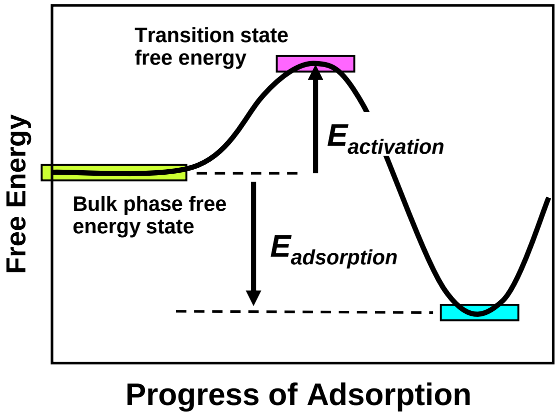

Fig. 3. Illustration of potential energy barrier that is often assumed to govern the progress of a chemical reaction, in which there is a transition state having less favorable energy than either the starting condition or the reacted (or bound) condition

Only a few articles were found in which activation energies were reported in the absence of proposed formation of covalent bonds. Dogan *et al.* (2009) reported an activation energy of 45.6 kJ·mol^{-1} for adsorption of methylene blue dye onto hazelnut shell material. Baral *et al.* (2006) reported 18 kJ·mol^{-1} for adsorption of Cr(VI) onto sawdust. Özer (2007) reported an activation energy of 30 kJ·mol^{-1} for the adsorption of lead ions onto wheat bran. However, in none of these cases is there a persuasive reason to expect there to be a significant energy barrier resisting the approach of the solute to sites of adsorption.

As a first step in shedding light on such processes, some researchers have used the temperature dependency of equilibrium adsorption capacities as a basis for estimating the potential energy associated with one mole of adsorption of various compounds onto cellulose-based substrates. However, as explained by Azizian *et al.* (2018), most reported results of such calculations have not employed dimensionless quantities, as is required by the logarithmic expressions used. To address this issue, Table 3 shows the results of dimensionally-consistent calculations based on three sets of published data dealing with physical adsorption from aqueous solution onto cellulosic materials or carbon.

To put the values in Table 3 into perspective, the average translational kinetic energy of each molecules, on a molar basis (3/2 x *RT*), is 3.7 kJ/mole at room temperature. Regardless of such results, many researchers have made the assumption that a good fit of adsorption data to the PSO model can be taken as evidence of chemisorption (Ho and McKay 1998c; Ho 2006a,b; Crini *et al.* 2007; Senthilkumaar *et al*. 2006; Ncibi *et al*. 2008; Xing and Deng 2009; Suteu *et al.* 2010; Nasir *et al.* 2018). Such assertions have been refuted (Tan and Hameed 2017).

Table 3. Recalculated Free Energies of Adsorption Obtained from Temperature Dependence of the Adsorption Capacity in Cases that also Showed Good Fits to the PSO Model

Temperature (K)	ΔG_{ad}° **(kJmol^{-1})**	ΔH_{ad}° **(kJmol^{-1})**	ΔS_{ad}° **(kJmol^{-1}K^{-1})**	**System Details**	**Literature Citation**
293	-6.71	-7.46	-0.0026	Ni(II) sorption onto nut shell active carbon	Demirbas *et al.* 2002
303	-6.69				
313	-6.66				
303	-12.41	-87.86	-0.249	Cu(II) sorption onto rubber wood sawdust	Kalavathy *et al.* 2005
308	-11.17				
313	-9.92				
298	-25.75	-27.83	-0.01	Phenol sorption onto activated carbon fibers	Liu *et al.* 2010
313	-25.62				
328	-25.43				

An inherent problem with models based on chemical reaction as a rate-limiting step in typical adsorption processes is that they generally consider only a “final” binding step rather than considering the likelihood of continual exchange between free and bound entities during the process of adsorption. Such interactions are well established, and in fact they form the basis for chromatographic measurements (Miyabe and Guiochon 2003). Because most of the cellulose-based adsorbent materials considered in different research projects can be expected to have relatively similar surface-chemical composition throughout their porous structure, no important differences are to be expected between a “final” site of adsorption (occupied at the end of the test period) and the surface sites occupied by an adsorbate species earlier in the adsorption process. Thus, there does not seem to be a valid reason to neglect transient adsorption from taking place in the course of the diffusion of species from the surface into the interior. Models that explicitly include transient adsorption during a process of diffusion of adsorbate into the pore structure of an adsorbent material will be considered in the next section (George and Thomas 2001; Rudzinski and Plazinski 2008; Douven *et al.* 2015).

Some of the earliest studies that employed the PSO relationship (Eqs. 4 and 5 presented earlier) can in fact be interpreted based on reactions involving covalent bonds. Thus, Ritchie (1977) set out to fit data related to gas adsorption onto solids by use of a generalized model involving an arbitrary reaction order *n*,

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \alpha(1-\theta)^{n} \qquad (11)$$

where θ is the fraction of occupied sites and α is a constant. When the exponent was set equal to 2, this expression was shown to fit data for several systems, including data from Bansal *et al.* (1971), who studied the rate of chemisorption of hydrogen onto carbon. In other words, the data fit well to the PSO equation. The use of an exponent of 2 can be justified in Eq. 11 if one assumes that the reaction requires dissociation of hydrogen, where the resulting adsorbed hydrogen atoms need to occupy two adjacent sites, and further that the adsorbed hydrogen atoms are able to diffuse while remaining attached to the surface (Medveď and Černý 2011). The envisioned situation is depicted in Fig. 4, where adsorption is assumed to be essentially bidentate, occupying two independent adjacent sites simultaneously (Wang and Giammar 2013).

While the PSO equation appears to be fully justified, if one accepts the stated assumptions for the system described, it is important to note that Bansal *et al.* (1971), as well as the other examples considered by Ritchie (1977) were considering situations in which covalent bonds were clearly involved. The early use of the PSO equation by Sobkowski and Czerwiński (1974) to fit adsorption data likewise involved a surface-facilitated chemical reaction as well as a surface partly filled with adsorbed atomic hydrogen, analogous to Fig. 4.

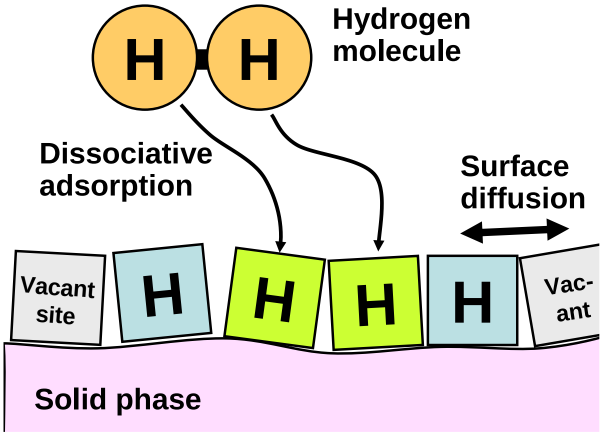

Fig. 4. Envisioned system, in which a PSO model might be justified, involving surface-catalyzed dissociation of H_2 molecules, where the progress is blocked by already adsorbed H atoms that are free to randomly hop to adjacent adsorption sites

Though the above-mentioned studies related to hydrogen adsorption and surface-mediated dissociation reactions appear consistent with a genuine PSO-related mechanism, it should be emphasized that these gas-phase reactions represent highly specialized cases. Unlike most studies of adsorption rates from aqueous solution, the just-cited studies all clearly involved a relatively large energy of activation to break a covalent bond.

Secondly, by use of a model resembling the game “musical chairs” (see Fig. 4) it was possible to justify the possibility that vacant sites on the surface might appear to diffuse randomly, which is another requirement of the PSO model, according to traditional chemical kinetics. For essentially physical adsorption from aqueous solution onto typical porous substrates, such as cellulose-based material, neither of these special circumstances are expected.

Studies Reporting Good Fits to Both Diffusion and PSO Models

Doubts can arise when two very different explanations are being offered to account for a single phenomenon. This is especially the case when the two explanations tend to contradict each other. Specifically, such a situation has arisen in many studies that have reported excellent fits to the PSO model also have reported good fits to models based on diffusion being the rate-limiting step. For instance, the studies listed in Table 4 all reported very high coefficients of determination for the PSO model, and they also showed good fits with the diffusion-based model proposed by Weber and Morris (1963).

Table 4. Listing of Studies Reporting Good Fits to the PSO Model and Also to Diffusion-based Systems such as the Weber-Morris Model

Experimental system	R^2 value for the PSO fit	Literature citation
Methylene blue onto wheat shells	0.997 to 0.998	Bulut & Aydin 2006
Methsufuron methyl onto volcanic soil	0.997 to 1.000	Caceres *et al.* 2010
Cu(II) and Pb(II) onto grafted silica	0.999	Chiron *et al.* 2003
Mn^{2+} onto biochar	0.999	Chowdhury *et al.* 2015
Methylene blue onto hazelnut shell	0.999 to 1.000	Dogan *et al.* 2009
Various studies compared	-	Douven *et al.* 2015
Methylene blue onto composite mixture	0.995	Liu *et al.* 2018
Malachite green onto rapeseed meal	0.980 to 0.981	Podstawczyk & W. 2016
Dye onto jute-derived carbon	0.991 to 0.999	Porkodi & Kumar 2007
Copper onto chitosan	0.995	Reddy & Lee 2013
Basic dyes onto peat-resin product	-	Sun and Yang 2003
Basic dyes onto activated carbon	0.999 to 1.000	Tan *et al.* 2008
Black dye onto nanocomposites	0.862 to 1.000 *	Tanzifi *et al.* 2018
Methylene blue dye onto rice husk	0.996 to 0.999	Vadivelan & Kumar 2005

* Note: The study by Tanzifi *et al.* (2018) compared four different integrated forms of the relationship for the PSO model, and quite different R^2 values were obtained, as shown.

A further problematic issue is that several authors, after reporting excellent fits to the PSO model, went on to explain their data based on concepts related to diffusion-limited processes (Sun and Yang 2003; Vadivelan and Kumar 2005; Bulut and Aydin 2006; Porkodi and Kumar 2007; Tan *et al.* 2008; Caceres *et al.* 2010; Reddy and Lee 2013; Podstawczyk and Witek-Krowiak 2016; Tanzifi *et al.* 2018). Based partly on such problems, the review article by Plazinski *et al.* (2009) draws the conclusion that the PSO model does not provide a reliable indication of which mechanistic step accounts for the rate-limiting process of adsorption in a given case. In such instances, one could argue that mechanistically sound models are often more useful to analyze adsorption data, even if the coefficients of determination are lower than that of, say, a PSO model.

OTHER WAYS TO ACCOUNT FOR GOOD FITS TO THE PSO MODEL

Up to this point in the article, the focus has been on the mechanistic explanations that usually would be associated with the PSO model, involving a rate-limiting step that is second-order with respect to the available surface sites. In light of the discussion in the previous section, the main goal of this section is to answer the question, "since the PSO model itself does not appear well supported by the literature, what other explanations might reasonably account for so many excellent fits of adsorption kinetic data to the PSO equation?"

There are two main strategies that researchers have used in published works to provide an explanation for good fits of adsorption data to pseudo-second-order kinetics. The first of these sets of strategies is mathematical or statistical, arguing that the good fits are merely a consequence of how random errors can be expected to affect the analysis of data. Such an approach can be used, for instance, to assert that apparent fits to a PSO model are actually attributable to an underlying pseudo-first-order (PFO) mechanism. The PFO mechanism appears to rest on a solid theoretical foundation (Lagergren 1898).

However, even a sound theory is valid in this case only if the surface interactions actually represent the rate-limiting step in the process. The second strategy is to look deeper into the diffusion-based theories and models of adsorption. This appears to be a very fruitful approach, given the widespread usage of the Weber-Morris (1963) system of analysis, which is based on diffusion concepts.

Mathematical Issues

Data obtained from assumed PFO model fits best to PSO model

The theoretical analysis presented by Azizian (2004) considers cases in which the initial bulk concentration of adsorbing species is either relatively low or high. By starting from the Langmuir kinetic model, it was found that when the bulk concentration is relatively high, such that it does not change significantly during the course of adsorption, good fits to the PFO (Lagergren) equation are obtained. On the other hand, when the initial bulk concentration is relatively low, such that it changes significantly during the course of adsorption, the PSO rate equation can describe the kinetics well. Thus, it was found that good fits to the PSO equation can be merely a consequence of mathematics and the selection of experimental conditions.

Another problem inherent in the PSO model, in its more commonly used forms (Blanchard *et al.* 1984; Ho and McKay 1998a; Ho 2014), is that it does not consider the possibility of a reverse reaction, *i.e.* desorption. Since almost all of the relevant studies have involved physical adsorption, rather than reactions to create covalent bonds, such neglect of desorption seems unrealistic. If both adsorption and desorption can occur, and the rates of exchange are high enough, then one can assume an equilibration between the bulk and surface sites during the whole process of adsorption. Chatterjee and Schiewer (2014) found that in cases where the initial concentration was high enough, their analysis based on continual equilibration of adsorbate molecules with surface sites was able to fit kinetic data. Azizian (2004) likewise included a desorption reaction in the analysis in an effort to develop a more realistic model while still emphasizing surface reactions during adsorption (Liu and Liu 2008).

Insufficient "early" data

A related problem, which affects many of the reported data sets that have given high values of R^2 for the PSO model, is that only a few of the data points represented relatively low values of exposure time (Canzano *et al.* 2012). Such "early" data points are critical when attempting to discriminate between a PFO and PSO model based on goodness of fit. When not enough data are obtained at relatively low times of contact between the solution and the adsorbent, the analysis becomes more highly dependent on conditions approaching equilibrium. As already mentioned, those later times can be expected to be most affected by both (a) the fact that the PSO model does not consider a reverse reaction (desorption), and (b) the difference between the initial bulk concentration and its final value will be the largest. Canzano *et al.* (2012) used numerical simulation to show that such considerations can lead to good fits to the PSO model when most of the data are obtained as systems are approaching an equilibrium level of adsorption. Notably, the simulation was based on random diffusion, rather than the mechanisms implied by the PSO equation.

Time-dependency reflected in both plotted axes

In an attempt to explain why, in so many cases the PSO model has provided very good fits to data, an additional suggestion is that this is due to involvement of the time variable in both of the plotted axes during the fitting procedure (Canzano *et al.* 2012; Tanzifi *et al.* 2018). The suggestion is that, by using the most favorable integrated form of the PSO relationship, all the R^2 values get shifted closer to 1.000. As was shown in Table 4, Tanzifi *et al.* (2018) obtained R^2 values in the range 0.862 to 1.000 depending on which of four integrated forms of the PSO model was employed.

Canzano *et al.* (2012) suggested that, to minimize the influence of conditions not fitting the assumptions of the PSO model, one should omit data nearest to the equilibrium point. This is a harsh requirement, since many researchers and engineers would be interested in what happens when adsorbent material is close to saturation.

In the authors' opinion, the best method for fitting on PSO model is non-linear fitting based on non-linear form of PSO equation:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{12}$$

This approach is preferred because it does not include any unrealistic requirement or involvement of time variable in both plotted axes.

Amplification of skewed errors (especially linearized fitting)

Several studies have shown cases in which fits to the PSO model were highly dependent on the selection of a mathematical expression, among the forms that have been derived (Vázquez *et al.* 2012; Tan and Hameed 2017). As noted earlier, four different expressions can be derived by integration of the differential equation expressing the PSO relationship (Ho 2006a,b), as listed in Table A in the Appendix. Sometimes the alternative expressions can give good agreement regarding the fitting parameters, even if the R^2 values are very different (Tanzifi *et al.* 2018). According to Canzano *et al.* (2012), the use of a linearized integrated form of the PSO relationship tends to give the greatest amplification of the effects of random errors, often giving rise to unmerited agreement with experimental data.

A flexible equation for fitting

The term "lumping of parameters" has been used in situations where a quantifiable phenomenon appears to have a complex dependency on a set of parameters due to interactions among more than one mechanism (Cosby *et al.* 1985; Chatterjee and Schiewer 2014). It appears that the PSO model, considering the manner in which it is commonly employed to fit adsorption data, can fit the definition of a lumping of effects (Tan and Hameed 2017). Specifically, rather than implying a specific reaction-dependent rate-limiting mechanism, a good fit due to the PSO model can have other interpretations, including diffusion-limited rate behavior (Douven *et al.* 2015). Such an explanation, due to its generality, lacks the potential to differentiate among various alternative contributing mechanisms. Rather, it has been said that the PSO model can be regarded as a flexible equation capable of fitting a range of typical adsorption kinetic data (Tan and Hameed 2017). According these authors, in light of the range of possible contributions to kinetic behavior, it is futile to use PSO fit information as a sole means of drawing conclusions regarding fundamental aspects of the process, and in particular, such fits do not provide evidence of chemisorption. In theory, one way to fit data might be with a combination of PFO, PSO, and desorption mechanistic steps. However, given the fact that the PSO model by itself is already capable of delivering R^2 values near to unity, it is hard to envision how the same data could be used to more fully understand rate behavior that can be attributed to multiple mechanistic steps.

Diffusion-limited Models

Two contrasting situations can be considered when discussing kinetic models based on diffusion mechanisms. On the one hand, as in typical covalent reactions, one envisions a process in which the reaction to form a compound (for instance, the attachment of a group to a surface) is essentially irreversible. Alternatively, one can assume that the adsorbing species can be in continual near-equilibrium with the surface, such that there is a predictable relationship between free and adsorbed populations. The discussion that follows will include an assumption that both adsorption and desorption will take place at finite rates in the course of the progress of adsorbate from the exterior surface to sites within the pore structure of the adsorbent. Thus, as will be discussed, the fraction of time during which an adsorbing species is temporarily bound to a surface sites needs to be accounted for when defining an effective diffusion constant.

Fick's theories

A basis for understanding essentially all diffusion-limited processes is provided by the fundamental equations of Fick (Fick 1855; Henriksen and Hansen 2008). Fick's first law, as expressed in Eq. 13, relates the local rate of transport of species with a gradient of concentration (Wu *et al.* 2009a).

$$J = -D\frac{\mathrm{d}C}{\mathrm{d}x} \tag{13}$$

In this expression, J is the flux of the species of interest at a given point, D is the diffusion constant (diffusivity), C is the concentration, and x is the position relative to the gradient of concentration.

Though certain systems to account for adsorption have been based on just Fick's first law of diffusion, a fuller accounting requires an additional relationship (George and Thomas 2001). Fick's section law can be expressed as in Eq. 14:

$$\frac{\partial C}{\partial x} = D\frac{\partial^2 C}{\partial x^2} \tag{14}$$

In a typical experimental situation, one can envision that the bulk concentration in solution will have a known concentration. When a known amount of adsorbent material is placed into such a solution at a time defined as zero, the corresponding concentration of adsorbate associated with the adsorbent material is also taken to be zero. So initially there will be a very strong gradient of concentration at the external surface of the adsorbent material. After a brief period of time, however, equilibration will have taken place with sites near the external surface, and a less-steep gradient of concentration will have progressed towards the interior of the particles of adsorbent (Rudzinski and Plazinski 2006).

One of the general expectations that follows from diffusion-limited rate behavior is that progress towards completion ought to be a function of the square-root of time (Weber and Morris 1963; Tan and Hameed 2017). However, there is another factor that needs to be considered before proceeding further. That is, Fick's laws, as expressed in Eqs. 13 and 14, are written in such a way that they imply a diffusion constant that is independent of location. In other words, a constant value of diffusivity is assumed at a given concentration of adsorbant in the adjacent solution (Chatterjee and Schiewer 2014). Such an assumption makes good sense in the case of diffusion within an isotropic liquid solution. However, in the case of a porous solid, diffusion can be constrained by physical barriers (*i.e.* pores extending mainly in just one direction), and the effective coefficient of diffusion being reduced by the fraction of time during which the diffusion species is immobile, in its adsorbed state. Within a smaller pore, the ratio between the surface area and the solution phase volume is larger, and such a situation favors a greater proportion of time in which a solute species is in an immobilized state at the surface.

As noted by Shen and Chen (2007), diffusion tends to dominate over convection as a means of mass transfer in zones of low permeability. Outside of such zones, depending on levels of agitation, pressure-driven flow, or thermal-motivated convection, *etc.*, solute species can migrate many times faster. Thus, the next issue to consider involves transport from bulk solution (usually assumed to be agitated) and the external surface of the grains, pellets, fibers, *etc.* that contain pores small enough to maintain essentially stagnant conditions within them.

External diffusion through a stagnant film or sublayer

Textbooks and articles describing ways to account mathematically for adsorption phenomena often begin by describing transport of adsorbing species from the bulk solution to an external surface across a film or boundary layer that is modeled as a stagnant layer of liquid (Boyd *et al.* 1947; Rudzinski and Plazinski 2008; Chatterjee and Schiewer 2014). This is illustrated schematically in the left side of Fig. 5.

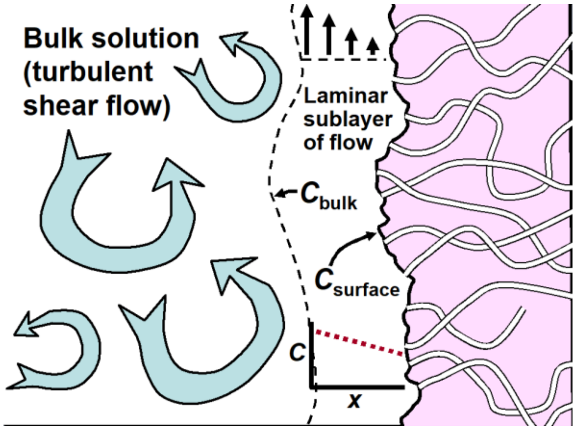

Fig. 5. Conceptual representation of a viscous sublayer at the surface of an adsorbent exposed to turbulent shear flow, such that there is a difference in the concentration of an adsorbate species between the bulk solution (at the dashed line) and at the external surface of the adsorbent

It has been shown that such transport may essentially stop if the bulk solution is unstirred (Weber and Morris 1963). In such cases, molecular diffusion by itself may be the only significant means of transport over relatively long distances, and molecular diffusion is a slow process. In view of this situation, it should not be surprising that practical systems of adsorption involve either the stirring of a suspension or the flow of solution through a packed bed. By such means, convection, which is a much more rapid mechanism of transport, can be relied upon to maintain the solute concentration near its bulk level adjacent to the particle surface. For instance, Weber and Morris (1963) demonstrated that the rate of adsorption onto porous material in a suspension depends on the rate of agitation only up to a certain speed of stirring, and thereafter the overall rate is independent of further increases in agitation. On the other hand, the overall rate of uptake is drastically reduced if stirring is discontinued.

Even if the bulk solution is stirred or pumped through a packed bed, there still will remain a film of liquid adjacent to the surface that can be modeled as a near-stagnant layer, such that it is reasonable to expect that transport across that layer to adsorption sites at an external surface will be governed by diffusion rather than by convection. The rate of transport in such cases, at least in the beginning, is expected to be proportional to the external surface area of the adsorbent (Chatterjee and Schiewer 2014). The cited authors concluded that processes following a pseudo-first-order rate of adsorption ought to fit well to a film-diffusion model as the rate-limiting step.

The right side of Fig. 5 represents a porous material within which diffusion is assumed to be the main mechanism of transport. In this kind of model it is assumed that any convection currents affecting the bulk of solution do not influence the interior of the adsorbate particles. Further, it usually is assumed that there is no intermittent squeezing and relaxing of the adorbate particles, which might otherwise cause flow in and out of a porous material.

Though most studies of adsorption phenomena have tended to focus on either the full process or conditions approaching equilibration or saturation, a study by Rudzinski and Plazinski (2008) concentrated on the very start of the process. A surface diffusion mechanism was found to be consistent with their data. The fact that their plots of adsorbed amount *vs.* square-root of time did not pass through the origin is consistent with an expectation that external surface film diffusion cannot account for the full process of adsorption. According to the theoretical analysis of Douven *et al.* (2015), diffusion rates associated with an external film can be expected to be important only in the very early phases of adsorption, and this factor will no longer play a significant rate-limiting role once the bulk solution has had time to equilibrate with the external surface region of the adsorbate.

Diffusion along a solid surface

The next topic, though less often mentioned in the published literature having to do with adsorption from solution onto solids (Boyd *et al.* 1947), will be considered at this point due to its similarity to the external boundary layer film concept just described. For the sake of the present discussion, this mechanism will be called "diffusion along a solid surface". The idea is that a solute species might be able to diffuse while remaining in contact with the surface (Alanissila and Ying 1992; Choi *et al*. 2001; Medveƌ and Černý 2011). According to Choi *et al.* (2001) surface diffusion can account for more than 50% of mass flow rate within certain microporous adsorbents. Figure 6 is based on a concept described by Medveƌ and Černý (2011) in which surface diffusion may involve the input of activation energy – not necessarily enough energy in each step to release the adsorbed species back into the bulk solution phase, but enough to mobilize it and allow it to randomly hop to a new location at the surface.

The surface diffusion concept has been employed as a contributing explanation in several various studies involving adsorption (Gutsche and Yoshida 1994; Maekawa *et al.* 1995; Choi *et al.* 2001). In particular, it is reasonable to expect that enzymes such as cellulase can remain attached to a cellulose surface while remaining in motion (Jervis *et al*. 1997; Zhang *et al.* 2016), though such motion may become constrained (Moran-Mirabal *et al*. 2013). Such systems have been discussed by Wu *et al.* (2009b). The surface diffusion mechanism can be expected to have relevance in cellulose-based systems due to the orientation of such structures as the fiber surfaces, lumen spaces, the local alignment of fibrils, and the slit-like shape of pores within cellulosic fibers after chemical pulping has removed most of the lignin. Such issues will be discussed in the final main section of this review article.

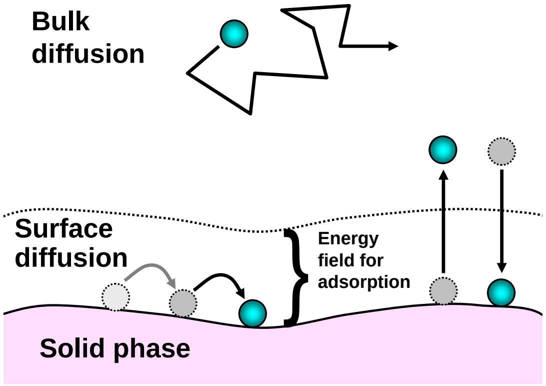

Fig. 6. Concept of surface diffusion involving a relatively low level of activation, allowing the adsorbate to hop to a random adjacent site of attachment

Crank's comprehensive diffusion-based analysis

As discussed by Rudzinski and Plazinski (2008), Chatterjee and Schiewer (2014) and Tan and Hameed (2017), one of the most complete systems to account for rates of adsorption in terms of contributing mechanisms was presented in the textbook by Crank (1956). It has been stated that other models, such as those of Weber and Morris (1963), Elovich (Piasecki and Rudzinski 2007; Liu and Liu 2008; Tan and Hameed 2017), and Boyd *et al.* (1947) can be regarded as restricted sub-models of the Crank analysis (Chatterjee and Schiewer 2014, see later discussion).

To summarize, the Crank model includes consideration of an external boundary layer (sometimes called surface film) diffusion step, which is assumed usually to be rapid relative to the subsequent steps of adsorption (Tan and Hameed 2017). The process of diffusion is understood to take place simultaneously with a faster exchange of adsorbing species between free and immobilized (adsorbed) states. In other words, both forward and reverse interactions with the surface are assumed to take place as the adsorbing species, on average, makes progress towards saturating the interior surfaces of the adsorbent. The Crank model is based on both Fick's first and second laws of diffusion, and thus it is able to deal with situations in which the local value of diffusivity is not constant.

As described especially in Chapter 8 of the cited work (Crank 1956), Crank assumes a fixed relationship between the local concentration S of immobilized adsorbate molecules or ions at the outer surface of the pellet and the local concentration C_p in the adjacent solution within a pore. This relationship can be expressed as,

$$S = RC_p \tag{15}$$

where R can be regarded as a partition coefficient between the adsorbed phase and the solution phase. Adsorption is assumed to take place continuously during the diffusion process, which is assumed to follow the diffusion-based relationship,

$$\frac{\partial C_p}{\partial t} = D\frac{\partial^2 C_p}{\partial x^2} - \frac{\partial S}{\partial t} \tag{16}$$

Substitution of Eq. 15 into Eq. 16 yields:

$$\frac{\partial C_p}{\partial t} = \frac{D}{R+1}\frac{\partial^2 C_p}{\partial x^2} \tag{17}$$

In this expression one can take the term [$D/(R+1)$] as an effective value of D, taking account of the degree to which the rate of diffusion is slowed down by the proportion of time that the solute is immobilized on the local surfaces.

Forward and reverse reactions with the surface, *i.e.* adsorption and desorption, can be expressed as,

$$\frac{\partial S}{\partial t} = \lambda C_p - \mu S \tag{18}$$

where λ and μ are the local rate constants for adsorption and desorption.

The validity of Crank's model is limited by the assumption of proportional adsorption, as recalled in Eq. (18). In addition, if one assumes that the amount of adsorbent is so low that the concentration of molecules in solution remains almost constant during the adsorption process, Douven *et al.* (2015) show that the solution of Crank's model can be written as:

$$\frac{n(t)}{n_{eq}} = 1 - \frac{6}{\pi^2}\sum_{m=1}^{\infty}\frac{1}{m^2}\exp\left(-\frac{D_e m^2 \pi^2 t}{R_p^2}\right) \tag{19}$$

In Eq. 19, $n(t)$ is the total number of adsorbed species at time t, n_{eq} is the equilibrium value of n after a long time of exposure, m is the mass of adsorbent, D_e is the effective diffusion coefficient (as affected by the fraction of time immobilized at surfaces), R_p is the radius of adsorbent particles, and the sum over m runs from one to infinity.

Douven's Langmuir adsorption-desorption (LAD) analysis

Douven *et al.* (2015) generalize Crank's approach by considering that adsorption is seldom conducted at concentrations so low that the surface is far from being saturated. The effect of saturation is accounted for by a Langmuir mechanism, by which the local rate of adsorption inside a pellet decreases when the concentration of immobilized species increases. This effect is absent in Eq. (18), which is equivalent to assuming proportionality between adsorbed and free molecules.

When one assumes that a Langmuir isotherm governs the adsorption process throughout a porous structure, the following equations can be used to predict the rates of adsorption and desorption,

$$\frac{\partial C_f}{\partial t} = D\Delta C_f - k_a C_f\left(1 - \frac{C_a}{C_{sat}}\right) + k_d C_a \tag{20}$$

$$\frac{\partial C_a}{\partial t} = +k_a C_f\left(1 - \frac{C_a}{C_{sat}}\right) - k_d C_a \tag{21}$$

where C_f is the concentration of adsorbate that is free in the pore-filling solution, D is the diffusion coefficient, Δ is the Laplace operator, k_a is the rate constant for local adsorption, C_a is the adsorbed concentration, C_{sat} is the adsorbed saturation concentration, and k_d is the rate constant for desorption. When time is extended to infinity, these equations imply the relationship,

$$\frac{C_a}{C_{sat}} = \frac{C_f}{vC_{sat}+C_f} \qquad (22)$$

which is just an expression of the assumed Langmuir equilibrium state.

The LAD approach proposed by Douven *et al.* (2015) can be regarded as an effort to apply a robust diffusion-based analysis that also takes into account reversible interactions with surface sites. A key feature of the analysis is the use of the Langmuir isotherm to mathematically describe the relationship between adsorption and the concentration of the adsorbate in the solution within each region within the system. As in Crank's (1956) analysis, Douven *et al.* (2015) make the assumption that both the forward and reverse interactions with the surface take place continuously as adsorbing species diffuse within pores of the adsorbent. The selection of the Langmuir isotherm for such fits can be justified based on their well-established theoretical foundation (Langmuir 1918). Also, systems of adsorbates and adsorbents that have been found to fit well to a Langmuir model generally have been judged to be promising with respect to suitability for efficient removal of various solutes from solution (Hubbe *et al.* 2014). Tan and Hameed (2017) noted that Douven's system can give excellent mathematical fits to data that also fit the PSO model.

A powerful aspect of the Douven *et al.* (2015) approach is its generality, which enables one to identify a variety of working regimes for any given adsorbate/adsorbent couple. These regimes can be identified through three dimensionless numbers: (i) an adsorption/diffusion modulus to determine whether surface reaction or diffusion is the rate limiting process (controlled by the size of the pellets); (ii) a saturation modulus to determine whether proportional or saturated Langmuir-like adsorption takes place (controlled by the concentration of the solution); and (iii) a loading modulus to determine whether the concentration of molecules in the solution decreases significantly in the course of the adsorption, or if it can be assumed to remain constant (controlled by the amount of adsorbent). In defining dimensionless parameters for such a situation, the cited work builds notably upon earlier progress achieved by Rudzinski and Plazinski (2008). It has, however, to be stressed that the dimensionless numbers defined by Douven *et al.* (2015) are related to the operating conditions, independently of the adsorbent material and adsorbate.

Douven *et al* (2015) notably show that the shape of the adsorption kinetic curves is controlled also by the operational conditions under which adsorption kinetics is being measured, in addition to the chemical nature of the adsorbent and adsorbate. This applies also to the suitability of phenomenological models such as the PFO and PSO models.

Douven *et al.* (2015) also established a procedure for data analysis based on evaluation of the measured "half-times" required for adsorption of half the full capacity into suspended pellets of adsorbent. For example, the PSO model is mathematically equivalent to the following equation,

$$\frac{n(t)}{n_{eq}} = \frac{t/t_{1/2}}{1+t/t_{1/2}} \qquad (23)$$

where the first term is the same as in Eq. 19, and $t_{1/2}$ is the time required for the adsorbed amount to reach half of its equilibrium value. This equation was found to fit well to experimental data, which is consistent with the wide empirical validity of the PSO model. Based on the general LAD model, Douven *et al.* (2015) tabulated the values of $t_{1/2}$ for a variety of operational conditions identified through the three dimensionless numbers, which enables one to determine the diffusion coefficient.

Weber-Morris intra-particle diffusion analysis

Among the diffusion-based systems of analysis, the "intraparticle diffusion" (IPD) model of Weber and Morris (1963) has been employed by far the most often for fitting of adsorption data in the case of porous materials. The following are a representative group of articles in which the Weber-Morris approach was employed to fit adsorption data (Waranusantigul *et al.* 2003; Suteu and Bilba 2005; Vijayaraghavan and Yun 2007; Mohan *et al.* 2008; Ofomaja 2008; Laohaprapanon *et al.* 2010; Nethaji *et al.* 2010; Rubin *et al.* 2010; Thirumalisamy and Subbian 2010). The governing equation can be expressed as,

$$q_t = k_{ipd}\sqrt{t} + C \tag{24}$$

where q_t is the adsorbed amount as a function of time (t), k_{ipd} is the rate constant for intra-particle diffusion, and C is a constant associated with the boundary layer thickness (*i.e.* the "film" for the external film diffusion model). As noted, the Weber-Morris system can be regarded as a subset of the Crank analysis (Chatterjee and Schiewer 2014; Douven *et al.* 2015). Unlike the comprehensive approach described by Crank (1956), Weber and Morris (1963) considered only diffusion aspects, without considering how transient adsorption of the adsorbate during the process might be expected to influence the effective value of the diffusion coefficient D.

A characteristic feature of the Weber-Morris (1963) approach is a predicted proportionality between the adsorbed amount and the square-root of time. This square-root relationship can be regarded as a "slowing down" of the adsorption rate in comparison to a linear, constant rate of uptake. In principle, if the adsorption data all can be described by a single line, when plotted *versus* the square-root of time, then the model can be taken to represent a single rate-limiting process of diffusion. In practice, such linear agreement seldom has been reported (Weber and Morris 1963). Rather, most researchers have been forced to conclude that the adsorption process, in numerous practical situations, is governed by more than one limiting mechanism – often three or more. Examples of this are provided in Table 5.

Table 5. Listing of Studies in Which Fits of Adsorption Data to the Weber-Morris Model Were Achieved by Use of Two or More Linear Segments

Experimental system	Number of linear segments	Literature citation
Herbicide onto volcanic ash	2	Caceres *et al.* 2010
Acid dye onto chitosan	3	Cheung *et al.* 2007
Basic and acid dyes onto wood *	*ca.* 2	Ho & McKay 1998b
Basic dye onto graphene oxide hydrogel	3	Liu *et al.* 2018
Dyes onto wood sawdust *	*ca.* 1 to 2	Ofomaja 2008
Copper (II) ions onto chitosan	3	Reddy & Lee 2013
Basic dyes onto peat-resin particles	3	Sun and Yang 2003
Amido black dye on nanocomposite	2 & 3	Tanzifi *et al.* 2018
Methylene blue onto rice husk	*ca.* 3	Vadivelan & Kumar 2005
Reactive dye on microbial biomass *	*ca.* 3	Vijayaraghavan & Yun 2007

* - These authors did not fit their data by regression. The numbers of line segments required were estimated based on appearance of the curves of uptake *vs.* the square-root of time.

The need to assume multiple mechanistic steps can be regarded as a weakness of this approach, since none of the cited articles made any effort to suggest the nature of these proposed other rate-limiting steps. In addition, the use of three or more segments of linear regression to fit a set of adsorption rate data limits the degrees of freedom in the analysis and weakens any possible conclusions, from a statistical perspective. When considering the excellent linear regression results that are often reported when presenting results from a Weber-Morris analysis, it is important to bear in mind that competing models, such as the PSO and PFO, for instance, would be expected to fit all of the data with a single expression.

A fascinating aspect of the experimental work considered by Weber and Morris (1963), who studied adsorption of alkylbenzene sulfonate onto activated carbons, is that allowing the adsorbent to "rest", which consisted for stopping the agitation for a period of 12 hours, appeared to restore an extra increment of adsorption capacity and corresponding higher rates of adsorption, compared to the same conditions without a rest period. These findings suggested to the researchers that the passage of time, without flow to facilitate a lot of fresh arrival of adsorbing species at the outer surface, allows for a net diffusion of solute farther into the interior of a fine network of pores. Also it was observed that adsorption continued almost linearly for many hours. Such issues may be important for various cellulose-based adsorbent materials, since they might influence whether there is a sufficient time of contact provided, in a given situation, to take advantage of the majority of the available adsorption capacity.

Boyd analysis

The kinetic analysis introduced by Boyd *et al.* (1947) can be regarded as a limiting case of the Crank analysis just discussed (Chatterjee and Schiewer 2014; Tan and Hameed 2017). The Boyd analysis, as commonly applied, provides a plotting procedure by which researchers can determine whether or not external diffusion from the bulk of solution plays a significant rate-limiting effect on the net adsorption (Vadivelan and Kumar 2005; Porkodi and Kumar 2007). In particular, the rate constant for external diffusion was plotted as a linear function of flow velocity adjacent to the surfaces.

Mechanisms considered by Boyd *et al.* (1947) were limited to (a) external diffusion through a film or boundary layer from the bulk of solution to the external surface of an adsorbent, (b) a pseudo-first-order ion-exchange interaction, and (c) diffusion through interior of the adsorbent material. Step (c) is essentially the approach of Weber and Morris (1963), as already discussed. Based on a combination of theoretical and experimental findings, Boyd *et al.* (1947) concluded that their data could be best explained in terms of just the two diffusion-based mechanisms. However, as noted by Liu and Liu (2008), the time-dependencies of the PFO model and the intraparticle diffusion mechanism were not sufficiently different to enable Boyd *et al.* (1947) to distinguish between them based on kinetic data. Boyd *et al.* (1947) observed that above a critical concentration the rate of adsorption in the system they studied appeared to be governed by intraparticle diffusion, whereas below that critical concentration the rate of adsorption was more affected by external diffusion.

Elovich analysis

The Elovich equation, which was originally presented by Roginsky and Zeldovich in 1934 (Liu and Liu 2008), can be expressed as,

$$\frac{\mathrm{d}q}{\mathrm{d}t} = a_E e^{-\alpha_E q} \tag{25}$$

in which a_E and α_E are constants. A derivation of the Elovich equation also was provided by Piasecki and Rudzinski (2007), who indicated that the Elovich equation followed from their "statistical rate theory". Basically, the Elovich model predicts an exponential decline in the rate of adsorption with time. Notably, the exponential term depends not only on time but also on the amount of adsorption at time t. This inclusion of the quantity q within the exponential term results in a predicted acceleration of the decrease in rate of adsorption, especially at low values of t when q would be expected to be increasing more rapidly. Douven *et al.* (2015) called the term α_E a "slowdown parameter." Chowdhury *et al.* (2015) reported data for adsorption of manganese ions on biochar that appeared to fit both the PSO equation and the Elovich equation. Other researchers finding good fits to the Elovich equation include Ho and McKay (1998c), Aretxaga *et al.* (2001), and Caceres *et al.* (2010). As the Elovich equation leads to a logarithmic growth of the amount of adsorbed molecules with time, it will never lead to a saturated condition. Therefore it can be regarded as an empirical model that describes just a part of the adsorption process.

Concept of a distribution of D values

A key limitation in the approaches that have been employed so far to predict adsorption rates based on diffusion models is that none of them have dealt explicitly with the heterogeneity of pore sizes in real adsorbents (Tan and Hameed 2017). The issue of heterogeneity in the local or time-dependent value of the diffusion constant D was already mentioned by Crank (1956) as a possibility. In principle, when there is significant affinity between a solute and the surfaces of an adsorbent, the effective value of D will decrease strongly with decreasing pore size (Douven *et al.* 2015). Thus, to make a convincing case to support a proposed rate expression, it would be desirable to be able to incorporate realistic estimates of the pore structure, including distributions of length of different sizes of pores. For instance in the case of water-swollen kraft fibers, one could assume (a) diameters and lengths of spaces between fibers in a pad, (b) pit opening sizes, (c) lumen diameters and lengths, (d) diameters and lengths of the larger mesopores in the cell walls, and (d) any further possible assumptions about either micropores or the possibility that the adsorbate species are able to diffuse through gel-like phases. Such a heterogeneous nature of pores in real materials, when viewed in the context of chromatography (Miyabe and Guichon 2003), would be expected to spread out the data, resulting in a long "tail" of very slow additional adsorption at very long times. Given the ever-increasing power of modern computers, rather than attempting to find integrated forms of rate expressions that can incorporate the complexities of diffusion and adsorption within realistic porous materials, it is suggested that researchers consider use of finite-element analysis and/or stochastic simulations to fit more complete diffusion models (*e.g.* as described by Crank 1956) to realistic estimates of pore structure in future work. Such approaches will be considered in the final main section of this article.

Reptation concepts

The term "reptation" can be defined as the snake-like motion of a chain-like polymer molecule within the constraints imposed by adjacent matter, which can include other polymer molecules (de Gennes 1971; Teraoka *et al.* 1992; Wu *et al.* 2009b; Hubbe *et al.* 2012a). Diffusion processes can be very slow when they require reptation (Wolterink *et al.* 2006; Wang and Luo 2007; Nam *et al.* 2010). Related phenomena can be expected in cases where pore sizes are sufficiently small that the adsorbing species are able to diffuse further down a passage only by changing their molecular conformation. Even greater slowing down of progress into a network of very fines pores can be expected in cases where the adsorbing species has to proceed one-by-one down a narrow pore leading further into the adsorbent material (Kabanov *et al.* 1989).

WHAT FITS TO PSO REVEAL ABOUT CELLULOSIC MATERIALS

This section of the article reviews published work to consider two possibilities. The first is to consider what is known about the pore structure of cellulosic materials. Such information may provide a basis for putting together a realistic model for mathematical simulation of diffusion in the pore structures of selected cellulose-based adsorbent materials. A second possibility is to consider factors for future experimental and simulation research related to the kinetics of permeation and adsorption into cellulose-based materials.

Deceleration of Adsorption Rates and What It Means

The word deceleration, for purposes of the present discussion, will mean that the rate of uptake slows down more rapidly that would be expected if the rate-limiting step involved the likelihood of collisions of adsorbing species with unoccupied sites at the surface of the adsorbent. In other words, “deceleration” will be taken to mean that the rate of uptake slows down with time to a significantly faster degree than would be expected based on the assumption of a pseudo-first-order (PFO) model (Douven *et al.* 2015). Some of the alternative ways in which such a deceleration in the adsorption rate can be expressed, as already reviewed in this article, include the PSO model (Blanchard *et al.* 1984; Ho and McKay 1998a,b,c; Ho 2006a,b) and a slowing-down factor in the Elovich equation (Douven *et al.* 2015). Of the factors already considered in this review article, two types of factors stand out as likely ways to explain the relatively strong deceleration of rates of adsorption with time, such that data more often agrees better with the PSO model than the PFO model. The two competing or contributing explanations are (a) significant depletion of the bulk concentration during a batch adsorption experiment, and (b) the requirement for longer periods of time for adsorbing species to diffuse to remote locations deep within a network of fine pores.

Deceleration of adsorption due to depleting of the bulk concentration

Azizian (2004) showed that both PFO and PSO equations can be derived from the Langmuir rate of equation. Based on this approach for derivation of the PSO equation, if the bulk concentration decreases, a deceleration of the adsorption rate is observed. The issue to consider at this point is to what degree this problem may affect researchers’ ability to use adsorption data in an attempt to understand cellulose-based materials.

A different problem arises if one attempts to overcome such problems just by increasing the initial bulk concentration. If the initial concentration is too high, then there will be a greater contribution of random error. Errors are amplified when subtracting two relatively large numbers (the initial and final concentration in the bulk) to be able to determine a smaller quantity (the amount that becomes adsorbed). The adsorbed amount is calculated using an expression such as,

$$S = (C_o - C_f)\, V / A \tag{26}$$

where S is the amount of adsorbed species per using area, C_o is the initial solution concentration, C_f is the final solution concentration, V is the volume of solution, and A is the area of adsorbate.

Another way to approach the situation is by numerical solution of the differential expressions, *i.e.* Eqs. 1 and 4. Here, since the integration has not yet been done, no assumptions have yet been made regarding the bulk concentration. The bulk concentration can be modeled using an expression such as,

$$C_o - C_t = S_t \, (A \,/\, V) \tag{27}$$

where C_t is the bulk concentration at an arbitrary time t and S_t is the adsorbed amount per unit area at time t.

Deceleration of adsorption due to increasing time to reach more remote pores

The second principal way to account for a deceleration of the rate of uptake, compared to the predictions of the PFO relationship, takes note of the fine pores and lack of convective flow within particles in a typical experimental or practical case of adsorption from solution. Whether or not the adsorbing species needs to undergo a reaction with the surface at the ultimate site of adsorption, there is no escaping the fact that to reach that position it must first diffuse either through the liquid or by surface-diffusion.

By contrast, it is not hard to visualize rapid interactions with the surface, in effect escaping from the necessity to regard this is a factor limiting the overall rate of adsorption. There are two aspects to this. First, as mentioned earlier, most of the situations of interest involve physical adsorption rather than the formation of covalent bonds. Accordingly, there is no reason to require a significant activation energy affecting the ultimate attachment. Second, there is likely to be a high ratio of surface area to solution volume within fine pores of the adsorbent. Any adsorbing entities present within the solution phase within a fine pore will be able to “try and try again,” maybe many times per second, to occupy adsorption sites at the surface.

Still considering the situation of an adsorbing entity within a tiny pore, deep within a cellulose-based adsorbent material, the high ratio or local surface area to solution phase will favor a high ratio of adsorbed entities, which implies a slowing down of the rate of progress. Factors that can further retard progress of achieving equilibrium saturation within the depths of a fine porous network can involve (a) charge repulsion between adsorbing species in the solution phase and an adsorbed one that is in the way of the first, or (b) physical blockage of the fine pore by an adsorbing species, blocking the progress of another one. The problem with such concepts is that they demand one to know a great deal about the details of pore morphologies within the nanostructure of the adsorbent. The next subsection considers how such information can be obtained, as well as some of the findings in the case of cellulose-based materials.

Linear lengths of pore structures within cellulose-based sorbent materials

The maximum lengths of pores structures, as listed in Table 6, are based on straight-line distances and known morphology. The lengths and diameters of fiber lumens shown in the table are as reported by Parham and Gray (1982) for the most-used species of wood. The length of a mesopore is merely an expression of half the thickness of a typical cell wall of a kraft fiber. The reason for selecting that distance, rather than the lengths of pores extended in the axial direction of fibers, is that much greater resistance to diffusion can be expected in the radial direction (Flynn 1995; Hansmann *et al.* 2002). The likely length of typical micropores within the cell walls of kraft fibers, depending on the level of refining, is expected to be substantially less than the thickness of a cell wall due to internal delamination of fibers due to such processes as swelling and refining (Molin and Daniel 2004).

Table 6. Estimates of Predominant Pore Lengths in Water-swollen, Chemically Pulped Wood Fibers, Activated Carbons, and Wood

Specimen type	Pore length	Citation
Chemical pulps – lumen spaces (hardwood species)	1 mm	Parham & Gray 1982
Chemical pulps – lumen spaces (softwood species)	3 mm	Parham & Gray 1982
Chemical SW pulps – mesopores (half cell wall thickness)	0.5-1 μm	Watanabe *et al.* 2000
Chemical SW pulps – mesopores (half cell wall thickness)	0.5-4 μm	Brandstrom 2001
Chemical pulps – micropores (<< cell wall thickness)	less	-
Granular activated carbons – mesopore (half particle size)	>400 μm	Perlach 1981
Powder activated carbons – mesopores (half particle size)	> 74 μm	Perlach 1981
Activated carbons – micropores (<< typical particle size)	less	-
Wood strands (in oriented strand board, OSB, thickness)	0.3-0.7 mm	Irle & Barbu 2010
Wood particles (in particleboard: thickness; length)	<10; 60 mm	Irle & Barbu 2010
Wood – lumen spaces (hardwood species)	1 mm	Parham & Gray 1982
Wood – lumen spaces (hardwood species)	3 mm	Parham & Gray 1982
Wood - micropores	less	-

The lengths of pores within wood can be estimated following similar principles. However, some key differences can be highlighted. In intact wood, the adjacent fibers are firmly bound together by a dense matrix of lignin and hemicellulose. The cell walls of wood likewise contain a higher density of solid matter, since there has been no removal of lignin. On the other hand, wood shares with kraft fibers a tendency to swell to some degree upon saturation with water.

The following sources have provided some information about the pores in typical wood specimens (Flynn 1995; Hansmann *et al.* 2002). One of the big uncertainties when attempting to model adsorption onto particles of wood is any tendency for the inherent structure to be torn open as the material is being converted to particulate form, as in the case of sawdust or ground wood material.

The length information in the case of activated carbon samples is again based on the reported dimensions of available powder products (Perlach 1981). It is reasonable to expect that the most effective grades of activated carbon will contain a diverse range of pores. The larger of them (perhaps the larger mesopores) will have a main job of allowing adsorbing species to reach interior regions, whereas the smaller of them (perhaps mainly micropores), will have the job of providing a very high surface area.

Diameters of pores within cellulose-based adsorbent materials

Table 7 shows some estimates of pore diameters within water-swollen kraft fibers, activated carbons, and wood based on various test methods. Determination of pore size is most often carried out by gas adsorption onto the dried materials, using the BET theory (Kaneko 1994).

Table 7. Estimates of Predominant Pore Diameters in Water-swollen, Chemically Pulped Wood Fibers, Activated Carbons, and Wood

Specimen type	**Analysis method**	**Pore diameter (nm)**	**Citation**
Chemical Pulp Fibers			
Review of various work, chemical pulps	Polyelectrolytes	100 & *ca.* 1	Alince 2002
Thermomechanical pulp (spruce) Unbleached kraft pulp (spruce) Bleached kraft pulp (spruce)	Solute exclusion, pullulans	0 to 3 0.5 to 7 1 to 10	Berthold & Salmén 1997
Wheat straw, soda-AQ pulp, freeze-dried	BET	2.5 to 6.3	Chen *et al.* 2010
Unspecified kraft pulps	NMR	11 to 17	Forsström *et al.* 2005
Bleached softwood kraft	NMR	8 to 18	Li *et al.* 1993
Bleached pine kraft	Solute exclusion	2 to 200	Stone & Scallan 1968
Pine and birch kraft pulps	NMR	11 to 17 & *ca.* 1	Suurnäkki *et al.* 1997
Activated Carbons	BET	1-2000	Perlach 1981
Macropores	-	> 50	IUPAC definition
Mespores	-	2 to 50	IUPAC definition
Micropores	-	< 2	IUPAC definition
Wood			
Lumens, Vessels	Microscopy	10,000+	Parham & Gray 1982
Macropores	-	> 50	IUPAC definition
Mespores	-	2 to 50	IUPAC definition
Micropores	-	< 2	IUPAC definition

As can be noted in Table 7, certain researchers have detected some pores in the wood pulp fibers that appear to be in the size range of less than 2 nm, *i.e.* micropores. Alince (2002) suggested that such micropores might actually be related to the non-freezing bound water, which typically can account for about 0.3 g per gram of water-swollen kraft fiber (Maloney *et al*. 1998). As an alternative to micropores, such water also may be envisioned as belonging to a hydrogel structure involving hemicellulose (Gabrielii *et al.* 2000).

Typical sizes of pores in commercial activated carbons are shown in Fig. 6, which is based on data in a plot from Perlach (1981). As shown, there is often a strong contrast between carbon adsorbent products intended mainly for gas adsorption and those intended for adsorption of compounds from liquid solutions. Activated carbons to be used in the gas phase mainly have micropores, *i.e.* pores having diameters less than about 2 nm. By contrast, activated carbons to be used as adsorbents in liquid media often have broad pore size distributions, not limited to micropores. The idea is that such a diversity should provide a balance between high surface area (contributed especially by micropores) and relatively quick diffusion into the interior of the adsorbent grains, pellets, or fibers (contributed especially by meso- and macropores).

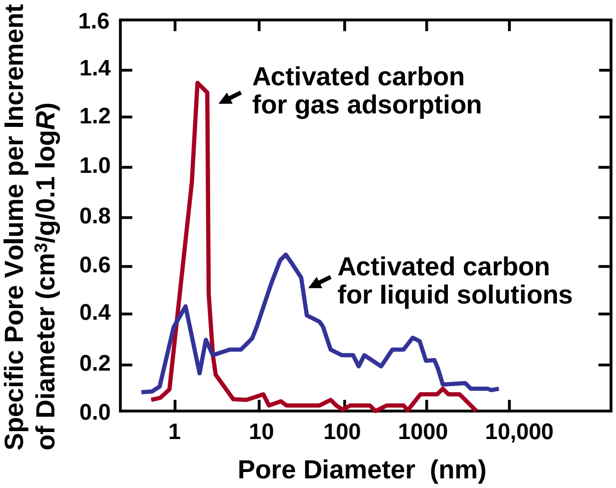

Fig. 6. Typical pore size distributions for activated carbons (based on Perlach 1981)

Potential for Analysis Using a Fuller Diffusion-based Model

In view of what is known about diffusion mechanisms and of the pore structures of cellulose-based adsorbent materials, there appear to be opportunities for carrying out more realistic numerical analyses. In particular, based on the literature it appears feasible to estimate the most predominant dimensions of pores within such adsorbent materials as activated carbons, water-swollen kraft fibers, and wood, *etc.* For example, it would be convenient to approximate the networks of pores within such adsorbents by models in which larger-diameter pores, having a distribution of lengths, lead to smaller-diameter pores, which also have a distribution of lengths. The diameters might be estimated, in different cases, based on the known nanostructure and by experimental methods. For example, in the case of bleached kraft fibers, the pore diameters and maximum lengths of each stage of diffusion could be estimated for (a) diffusion in the spaces between fibers, (b) diffusion within lumen spaces within fibers, (c) diffusion within mesopores in the cell walls, and (d) diffusion within micropores or within gel-like material yet deeper within fiber cell walls.

Figure 1, near the start of this article, provided a simplified, schematic concept in which diffusion into a porous material can be envisioned as a series of larger pores branching at distributed locations into a narrower class of pores, which have a distribution of branches into yet smaller pores. These might correspond to lumens or spaces between fibers in a mat of kraft fibers leading to mesopores in the cell walls, and then leading to micropores in the cell walls. Or in the case of activated carbon, they could correspond to spaces between particles in a packed bed, mesopores in the particles, and micropores branching in distributed fashion from the mesopores. Data from Tables 6 and 7, together with any other morphological information that may be available, would then complete the structural model.

Following from the descriptions of pore size distributions in cellulose-related materials (*e.g.* kraft fibers, activated carbon, wood, *etc.*), a case often can be made to model adsorption in terms of a series of stages. This concept is illustrated in Fig. 7.

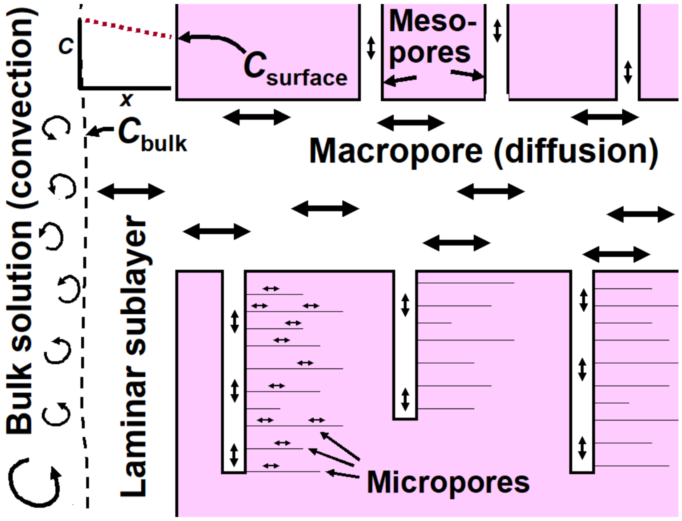

Fig. 7. Scheme to justify a stage-wise diffusion model. As described in the next section, the effective diffusion constant is likely to be significantly lower as pores become smaller.

The model depicted in Fig. 7 is set up with the following features:

A. Convective mixing (*e.g.* turbulent flow) in the bulk phase of solution outside of the laminar sublayer; the concentration of adsorbate is assumed to be uniform within the bulk solution.

B. Diffusion transport within the laminar boundary layer adjacent to the adsorbent material. The concentration of adsorbate is often modeled as decreasing in a linear fashion within this layer.

C. Diffusion within macropores (*e.g.* small spaces between fibers, lumen spaces within fibers, large pores). The adsorbate is assumed to equilibrate with the surface during the course of diffusion. Mesopores branch from the macropores at either random or evenly spaced intervals.

D. Diffusion within mesopores (*e.g.* cell wall or activated carbon spaces having diameters in the range 2 to 50 nm). Again, the adsorbate is assumed to equilibrate with the surface during the course of diffusion. Micropores branch from the macropores at either random or evenly spaced intervals.

E. Diffusion within micropores (*e.g.* cell wall or activated carbon spaces having diameters less than 2 nm). Again, the adsorbate is assumed to equilibrate with the surface during the course of diffusion.

Within the scheme just presented, it is to be assumed that within each region the adsorbate is undergoing continual equilibration with surface sites. This is illustrated in Fig. 8, which envisions a stagnant solution within macropore spaces, including fiber lumens and small spaces between fibers in a wet mat of pulp.

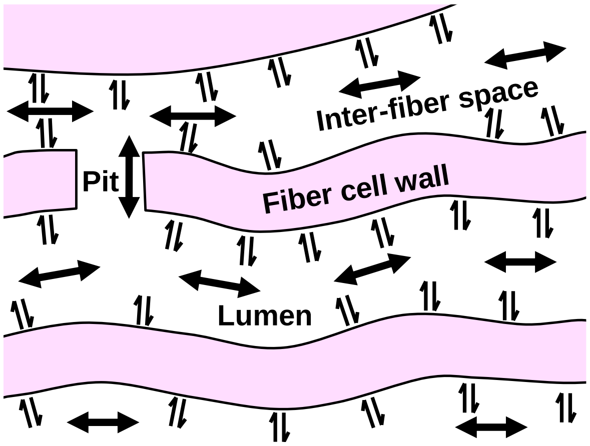

Fig. 8. Concept of simultaneous diffusion (represented by bold, two-ended arrows) and reversible adsorption (represented by equilibration symbols) during the permeation of an adsorbent into the spaces between fibers and lumen spaces (assumed to be essentially stagnant in this example)

Effective diffusion constant

The next step to consider may involve estimation of an effective diffusion constant pertaining to the rate of progress of the adsorbate through different regions of the adsorbent, *i.e.* lumens *vs.* smaller pores. Already it has been mentioned how the systems of Crank (1947) and Douven *et al.* (2015) deal with this issue – based on a partition coefficient or Langmuir isotherm, respectively.

In addition, an adjustment to the value of the parameter D could be used to account for the fact that a given pore structure might twist and turn, rather than proceeding straight into the interior of the adsorbent. In other words, an adjustment in the effective value of D can be used to account for the effect of tortuosity (Vanbrakel and Heertjes 1974; Epstein 1989; Leyvaramos and Geankoplis 1994; Shen and Chen 2007; Wu *et al.* 2009b). Heterogeneity of pore size is another factor that is likely to be play a large, but hard to quantify role in constraining the overall rate of diffusion rates and access to surfaces within porous media (Haggerty and Gorelick 1995). The cited study accounted for heterogeneity by considering an overall process of diffusion as being the sum of sequential sub-process in which the effective diffusion coefficient was not the same. They noted that some adsorbent materials can be regarded as a heterogeneous mixture, in which the mass transfer processes are not the same in different layers or "pods". Equation 28 was used by Vanbrakel and Heertjes (1974) to show the relationship between the effective diffusion coefficient and the relative pore volume (ε), a constriction factor (δ), and the tortuosity (ratio of diffusion path length to straight distance into the adsorbent, τ):

$$D_{\mathrm{eff}} / D = \varepsilon\, \delta / (\tau)^2 \tag{28}$$

Despite the simplicity of Eq. 28, it does not seem yet to have become well used as a means to account for rates of adsorption into porous materials.

Affinity of adsorbate to adsorbent

By analogy to chromatographic analysis methods, the time required for a physically adsorbing species to pass through porous materials can be expected to depend on its degree of affinity for surface sites (Tijssen *et al.* 1993; Miyabe and Guiochen 2003). A solute having little affinity for the column wall or the packing material generally will elute relatively quickly. A more strongly adsorbing species will elute more slowly. Though the situation is often different, depending on the details of the adsorption rate experiments, with the focus on the regions not experiencing a net flow of solvent, the same principle of slower progress is predicted by the analysis of Douven *et al.* (2015), where the degree of affinity is modeled based on a Langmuir isotherm. It follows that, in addition to depending on the sizes, tortuosity, and pinch-points within the pore structure, one should also expect adsorption rates to depend on the chemical nature of the surfaces and any forces or attraction or repulsion with the adsorbing species.

Depending on the nature of the lignocellulosic source material, as well as processes such as pulping, bleaching, solvent extraction, or chemical modification, the surfaces within cellulose-based adsorbent materials can vary greatly. Differences in affinity for water when comparing the surfaces of different lignocellulosic components can be determined by means of contact angle measurements with probe liquids (Hubbe *et al.* 2015). Lignin, which has a relatively high elemental proportion of C and H and a relatively low proportion of oxygen, is the most hydrophobic of the main components of biomass materials. By contrast, hemicellulose, which has an amorphous nature and an abundance of –OH groups, along with some carboxylic acid groups, is the most hydrophilic. The cellulose component, which has a high degree of internal-directed hydrogen bonding and crystalline nature, is intermediate with respect of its affinity for water.

Charge interactions

The negatively charged ionic groups associated with biomass, especially the hemicellulose component and some of the extractives, have great relevance to the adsorption of charged materials such as metal ions and dyes (Hubbe *et al.* 2011, 2012a). The subject of negatively charged groups associated with cellulosic material also had been studied (Budd and Herrington 1989; Hubbe *et al.* 2012b).

Adsorption of cationic substances onto predominantly negative materials often can be well described in terms of ion exchange (Boyd *et al.* 1947; Blanchard *et al.* 1984; Wågberg *et al.* 1988; Rengaraj and Moon 2002; Ho 2006a,b). In ideal cases the counter-ions on an anionic material used for ion exchange would be low-affinity monomeric species such as Na^+. Such monomeric metal ions are readily displaced by cationic substances having greater affinity, such as divalent lead or copper ions (Blanchard *et al.* 1984; Ho 2006a,b; Piasecki and Rudzinski 2007; Hubbe *et al.* 2011), or cationic dyes (Sun and Yang 2003; Porkodi and Kumar 2007; Hubbe *et al.* 2012a). However, the acidic sites on plant materials, when in contact with natural environments, may already be associated with calcium or other divalent ions (Momoshima and Bondietti 1990; Torre *et al.* 1992). Divalent ions are generally less susceptible to being replaced from adsorption sites on a charged surface (Wachinski 2017). Based on this example, the initial state, in terms of counter-ions, can be expected to affect the adsorption of cationic substances onto cellulosic materials. Since this topic has not been widely studied relative to the adsorption on cellulosic materials, there is a need for research in this area.

Solubility parameters

The principles of solubility provide another framework by which to understand the relative affinity of different adsorbates onto surfaces, especially in cases where ionic charges do not play a dominant role. As discussed by Hansen (2007), the tendency of a component to dissolve in a selected solvent can be predicted by comparing the Hildebrand parameters (square-root of the cohesive energy density), the polarities, and the hydrogen bonding capabilities. Highest solubility is expected when all three of these characteristics are close matches between the substance of interest and a given solvent. It has been proposed that the same relationship ought to be useful when predicting relative affinities of various compounds onto surfaces (Browne and Cohen 1993; Tijssen *et al.* 1993; Wang and Shi 2010). However, there appears to be a need to explore whether such concepts can contribute to a fuller understanding of rates of adsorption or absorption onto or into cellulose-based materials.

Reversibility

Based on the concepts of Crank (1956) and Douven *et al.* (2015), one can expect there to be marked differences in rates of permeation of an adsorbate species into porous material depending on the proportion of time that the species is immobilized at surfaces. It follows that the rate of desorption and the half-life of the adsorbed state will play important roles. Though many studies have considered procedures to displace adsorbed species back into solution – usually as a means to restore the adsorption capacity of an adsorbent material – few studies have attempted to evaluate the rate constants for desorption when factors such as pH and ionic strength are held constant. Thus, to gain a better understanding of overall adsorption kinetics, there is a need for careful analysis of desorption rates. As one approach, tests can be undertaken in which the bulk solution is suddenly replaced with fresh solution that is initially free of the adsorbate of interest.

CLOSING COMMENTS

At the beginning of this article the question was posed about what can be learned from the fact that a great majority of typical adsorption data, including data related to cellulosic adsorbents, can be fit to a pseudo-second-order (PSO) rate expression. The first part of this review article attempted and failed to find adequate support in the literature for the usual mechanistic assumptions that would be associated with the PSO model. Those findings provided a motivation to answer the following question: “How else can one explain the preponderance of excellent fits of adsorption data to the PSO model in many published studies?” Two kinds of contributing explanations have been considered in the course of this literature review, one based on a surface reaction acting as the rate-limiting step, and the other based on a diffusion-limited mechanism. Much of the evidence points to the diffusion-based mechanism playing a dominant role in typical cases. Also, it appears that continual equilibration of adsorbate with surface sites in the course of diffusing with pores offers a more realistic account of what usually is happening.

If one makes the assumption that the ultimate attachment of adsorbing species to adsorption sites is the rate-limiting step, then the literature suggests that a pseudo-first-order (PFO) rate would be most logical (Lagergren 1898; Douven *et al.* 2015). The fact that data more often fit better to a PSO rate expression implies that the rate of uptake slows down to a greater extent than one would expect based on the mere filling of adsorption sites. Of the several contributing explanations, one of the most persuasive involves the selection of experimental conditions. The adsorption rate data obtained for a process truly governed by a PFO mechanism can be expected to fit better to a PSO model if the initial pulp concentration is not high enough (Azizian 2004) and when there is a paucity of data associated with relatively short adsorption times (Canzano *et al.* 2012). To minimize such problems, while still attempting to achieve high precision, the initial bulk concentration needs to be chosen with care. Too high an initial concentration makes it harder to quantify how much solute has been adsorbed at any given time, since that quantity is usually calculated from the change in bulk concentration. But lower values become less and less consistent with the assumptions under which the PFO and PSO equations originally were derived, *i.e.* assuming that the bulk concentration is effectively constant.

The problems just described can be overcome if one assumes that any interactions of adsorbate and surface happen more rapidly than the unavoidable and time-consuming processes of diffusion. In particular, one can expect relatively longer times required for species to adsorb into the smallest of the pores and the pores situated deepest within the adsorbent material. Diffusion processes often can be regarded as a series of stages, including diffusion from the bulk solution across a boundary layer or film to the external surface of an adsorbent, diffusion within relatively large pores, diffusion within smaller pores, and finally within either micropores or a gel-like or solid-like material. If the adsorbate has an affinity for the adsorbent material, such affinity is expected to slow down the progress of diffusion, especially in the very small pores.

With modern computing power there will be opportunities to fit data without a need to place severe restraints on initial bulk concentrations. The pore sizes and lengths within cellulose-based and cellulose-derived (such as activated carbon) sorbents can be estimated by various means and then used as the basis to numerically fit the observed adsorption data based on quantifiable adsorption relationships, such as the Langmuir equation (Douven *et al.* 2015). Another challenge will be to evaluate desorption rates and/or half-life data for the adsorbed state into models to predict rates of adsorption into porous materials. Finally, there will be a challenge to quantify affinity information as a means of predicting such adsorbed half-lives into surfaces that can include cellulose, hemicellulose, and lignin (Hansen and Björkman 1998). In addition, many of the concepts explored in this review article will have application in understanding adsorption rates onto and into other kinds of porous substrates. All of these challenges can provide worthy topics for graduate thesis projects in the coming years.

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APPENDIX

Table A. Listing of Equations to Fit Adsorption Kinetic Data

Equation name	**Equation**	**Eq. #**	**Selected references**
Pseudo-first-order, differential form	$\frac{\mathrm{d}q}{\mathrm{d}t} = k_1(q_e - q)$	4	Lagergren 1898
Pseudo-first-order, integrated form	$\ln(q_e - q_t) = \ln q_e - k_1 t$	5	Tanzifi *et al.* 2018
Pseudo-second-order, differential form	$\frac{\mathrm{d}q}{\mathrm{d}t} = k_2(q_e - q)^2$	1	Blanchard *et al.* 1984; Ho 2006b
Pseudo-second-order, integrated form (“Type 1”)	$\frac{\theta}{1 - \theta} = k_2 t$	3A	Sobkowski & Czersiński 1974; Ho 2006b
Pseudo-second-order, integrated form (“Type 2”)	$\frac{q_\infty}{q_\infty - q} = \alpha t + 1$	3B	Ritchie 1977; Ho 2006b
Pseudo-second-order, integrated form (“Type 3”)	$\frac{1}{q_o - q} - \alpha = k_2 t$	3	Blanchard *et al.* 1984; Ho 2006b
Pseudo-second-order, integrated form (“Type 4”)	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	3D	Ho 2006 (from 1995 thesis)
Pseudo-second-order, integrated form	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$ or $q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$	12	Canzano et al. (2012)

Definitions:

α = a coefficient
k_1 = rate constant for a first-order reaction
k_2 = rate constant for a second-order reaction
t = time
q = adsorbed amount
q_e = adsorbed amount at equilibrium
q_t = adsorbed amount at time = t
q_∞ = adsorbed amount at infinite time
θ = fraction of available sites that are occupied

ERRATUMS

August 7, 2019:

Equation 7 was changed from “$d(AB)/dt = k\,[A]\,[B]$” to “$d[AB]/dt = k\,[A]\,[B]$”

Equation 8 was changed from “$d(AB)/dt = k'\,[B]$” to “$d[AB]/dt = k'\,[B]$”

Equation 10 was changed from “$d(A_2)/dt = k\,[A]^2$” to “$d[A_2]/dt = k\,[A]^2$”

Equation 16 was changed from “$\frac{\partial C}{\partial t} = D\frac{\partial^2 C_p}{\partial x^2} - \frac{\partial S}{\partial t}$” to “$\frac{\partial C_p}{\partial t} = D\frac{\partial^2 C_p}{\partial x^2} - \frac{\partial S}{\partial t}$”

Equation 17 was changed from “$\frac{\partial C}{\partial t} = \frac{D}{R+1}\frac{\partial^2 C_p}{\partial x^2}$” to “$\frac{\partial C_p}{\partial t} = \frac{D}{R+1}\frac{\partial^2 C_p}{\partial x^2}$”

Equation 25 was changed from “$\frac{dq}{dt} = a_E e^{-\alpha_E q_t}$” to “$\frac{dq}{dt} = a_E e^{-\alpha_E q}$”

June 28, 2021:

In the Appendix, the parameter *t* had been erroneously in the denominator on the right-hand side for the “Type 4” version of the integrated form of the PSO equation. The parameter *t* has been moved to the numerator. Thank you to Dr. Stefano Brandani for finding this error.