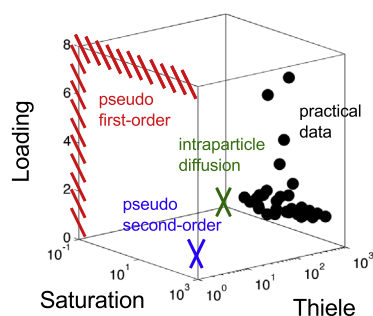# The range of validity of sorption kinetic models

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GRAPHICAL ABSTRACT

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ABSTRACT

Several hundred papers are published yearly reporting liquid-phase adsorption kinetics data. In general the data is analyzed using a variety of standard models such as the pseudo first- and second-order models and the Intraparticle-Diffusion model. The validity of these models is often assessed empirically via their ability to fit the data, independently of their physicochemical soundness.

The aim of the present paper is to rationalize the analysis of liquid-phase adsorption kinetics data, and to investigate experimental factors that influence the adsorption kinetics, in addition to the characteristics of the adsorbent material itself. For that purpose we use a simple Langmuir adsorption–diffusion model, which enables us to identify three dimensionless numbers that characterize the working regime of any batch adsorption experiment: an adsorption Thiele modulus, a saturation modulus, and a loading modulus.

The standard models are found to be particular cases of the general adsorption–diffusion model for specific values of the dimensionless numbers. This provides sound physicochemical criteria for the validity of the models. Based on our modeling, we also propose a general yet simple data analysis procedure to practically estimate the diffusion coefficient in adsorbent pellets starting from adsorption half-times.

1. Introduction

The importance of liquid-phase adsorption in porous materials for a variety of practical applications can hardly be overemphasized. This applies notably to water treatment, to liquid phase separation, to chromatography, among others [1–3]. Accordingly,

the development of synthetic adsorbent materials, as well as the testing of natural materials for adsorption processes, is an area of extremely active research.

The characterization of adsorbent materials and the assessment of their suitability for any given application requires the determination of both their equilibrium and kinetic properties. The reporting of adsorption equilibrium properties is generally not problematic because it is comprehensively described by the adsorption isotherm. By contrast, adsorption kinetics data depend

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on a variety of experimental factors that are seldom reported in the literature with sufficient care to make their analysis unambiguous, even in highly cited articles.

A common example is the situation where kinetic data are reported alone, without the corresponding equilibrium adsorption isotherm. In this case, it is impossible to analyze meaningfully the adsorption kinetic data, if only because it is unknown whether the experiments were done in the regime of saturated or proportional adsorption. This is one observation among many others, which lead us to believe that the experimental factors influencing liquid-phase adsorption kinetics are overlooked by many researchers in the field. The main goal of the present paper is to provide a systematic analysis of all the experimental factors that play a role in adsorption kinetics. In particular we define dimensionless numbers that are necessary to ascertain the relative importance of all these effects. These numbers are expressed in terms of variables, some of which are material (diffusion coefficient, concentration at saturation, etc.) and others are operating (size of the pellets, the volume and initial concentration of the solution, etc.). The definition of the dimensionless numbers enable one to analyze in a synthetic way the interplay of both types of variables. We also review the existing literature to calculate typical values of these numbers, in those relatively rare instances where all the necessary information has been made available in the publication.

An additional difficulty related to adsorption kinetics pertains to the use that is made of mathematical models for data analysis. Ideally, the role of mathematical modeling should be to simplify the apparent complexity of experimental data by determining the numerical values of a few material parameters with sound physicochemical significance. The model, together with meaningful material parameters, could then be used to extrapolate the results to experimental conditions more relevant to practical applications of the adsorbent. However, due to the availability of many different mathematical models for describing adsorption kinetics, a different situation is often encountered. In too many papers, a given adsorbent is tested for adsorption in a variety of conditions – different pellet size, stirring rate, solution concentration, etc. – and a variety of models are used to analyze *each and every* dataset e.g. [4–10]. In these conditions, the modeling adds to the complexity of the experimental data rather than simplify them. Because every measurement generally leads to a different value of the parameters of the models, this type of work provides very little physicochemical insight and it does not even enable one to extrapolate the data for any practical purpose [11]. In the present paper, we show that the applicability of many of the commonly used models can be discussed meaningfully in terms of the dimensionless numbers mentioned earlier. In other words: whether one model applies or another depends mostly on the conditions under which adsorption kinetics is being measured, rather than on the adsorbent material being tested.

A great many models have been developed since the end of the nineteenth century to analyze adsorption kinetics in liquid phase [12]. Their thorough discussion can be found in comprehensive reviews [13,7] and is beyond the scope of the present paper. We shall here merely highlight the different adsorption phenomenologies corresponding to four of the most commonly used models, namely the first and second-order Lagergren models, sometimes referred to as the pseudo-first and pseudo-second order models, the so-called Intraparticle-Diffusion (ID) model, and the Elovich model.

The vast majority of published adsorption kinetics studies make use of variants of the historical Lagergren model [14]. In the context of the first-order model, the convergence towards equilibrium is exponential:

$$\frac{dn}{dt} = k_1 \left(n_{eq} - n(t) \right) \tag{1}$$

where $n(t)$ is the quantity of molecules adsorbed at time t, say in mmol/g of adsorbent, n_{eq} is the equilibrium value, and k_1 is a first-order time constant. From a physicochemical point of view, first-order models are expected only if adsorption is limited by the transport of molecules from the solution to the adsorbent (film diffusion) [2] or when transport is not rate-limiting at all [15]. Therefore the constant k_1 is only phenomenological. The characteristics of the first-order model are plotted in Fig. 1.

In most kinetic data, the slowing down of adsorption with time is much sharper than predicted by the first-order model. A modified second-order model is therefore generally used, which consists in replacing the right-hand-side of Eq. (1) by $k_2[n_{eq} - n(t)]^2$, where k_2 is a second-order constant (see Fig. 1). The application of this type of model has notably been reviewed by Ho and McKay [16]. The popularity of this model is such that among the 5000 papers in the Scopus database that currently report liquid-phase adsorption kinetic data, more than 4500 of them use this second-order model. From a physicochemical perspective, a second-order adsorption kinetics can be justified in the case of specific adsorption mechanisms [17] or for specific working conditions [15]. However, most of the time the second-order adsorption is used as an empirical model that describes the data well. This procedure reduces the kinetic data to a single constant k_2 having no sound physicochemical meaning.

A third model that is sometimes used to analyze adsorption kinetics data is the following Elovich equation

$$\frac{dn}{dt} = k_E e^{-a_E n(t)} \tag{2}$$

where k_E is the initial adsorption rate and a_E is a constant that describes the slowing down of the process. Because this equation leads to a logarithmic growth of $n(t)$ with time, which does never saturate, it is necessarily an empirical model that describes only a small fraction of the adsorption process (Fig. 1). The fact that the Elovich equation is occasionally used to analyze data [18,19] illustrates the fact that adsorption kinetics can be extremely slow, to such an extent that they seem never to reach equilibrium.

Finally, the last model that we mention here is the so-called Intraparticle-Diffusion model [20], the origin of which can be tracked back to the work of Crank [21]. That model is the closest to the spirit of the present paper. It is based on a rigorous mathematical analysis of diffusion and adsorption of molecules inside a spherical pellet; it leads to the following expression for the total quantity adsorbed

$$\frac{n(t)}{n_{eq}} = 1 - \frac{6}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \exp\left(-\frac{D_e m^2 \pi^2 t}{R^2} \right) \tag{3}$$

where R is the radius of the pellet and D_e is an effective diffusion coefficient of the molecules in the adsorbent. For short times t, Eq. (3) predicts an asymptotic regime where the adsorption is proportional to the square root of time as follows

$$\frac{n(t)}{n_{eq}} = 6 \sqrt{\frac{D_e t}{R^2 \pi}} \tag{4}$$

This specific time-dependence is generally considered to be the signature of diffusion limitations (Fig. 1b). Eq. (4) has often been used to analyze adsorption kinetics data to determine the effective diffusion coefficient D_e [22,23], as notably reviewed by Wu et al. [24]. Although the Intraparticle-Diffusion model is based on sound physicochemical grounds, its strict conditions of applicability are more stringent than is usually acknowledged. Its conditions of applicability can also be expressed in term of the dimensionless numbers that we introduce in the present paper.