Insight into the adsorption kinetics models for the removal of contaminants from aqueous solutions

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ABSTRACT

The past decade has seen a boom in environmental adsorption studies on the adsorptive removal of pollutants from the aqueous phase. A large majority of works treat kinetic modeling as a mere routine to describe the macroscopic trend of adsorptive uptake by using common models, often without careful appraisal of the characteristics and validity of the models. This review compiles common kinetic models and discusses their origins, features, modified versions (if any), and applicability with regard to liquid adsorption modeling for both batch adsorption and dynamic adsorption systems. Indiscriminate applications, ambiguities, and controversies are highlighted and clarified. The appropriateness of linear regression for correlating kinetic data is discussed. This review concludes with a note on the current scenario and the future of kinetics modeling of liquid adsorption.

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1. Introduction

Adsorption is one of the most widely used technologies for removing pollutants from contaminated aqueous media. It is preferred over other methods because of its relatively simple design, operation, cost effectiveness, and energy efficiency [1]. The importance of adsorption for water and wastewater treatment is growing in view of the presence of emerging contaminants, such as pharmaceuticals and personal care products (PPCPs), in water bodies [2,3].

Water pollutants in the environmental adsorption literature can be generally categorized into six groups: (i) heavy metals, (ii) phenolics, (iii) dyes, (iv) pesticides, (v) PPCPs, and (vi) others (hydrocarbons, inorganic anions, etc.). These pollutants are found dissolved in water and wastewater in various concentrations. Numerous solid adsorbents with wide-ranging characteristics have been developed for removing these dissolved pollutants [4–9]. Basic classes of adsorbents include activated carbon, zeolite, clay, mesoporous silica, polymeric resin, and metal-organic frameworks.

The design and scale-up of an adsorption system require knowledge of adsorption equilibrium and kinetics. The development of kinetics understanding is largely limited by the theoretical complexity of adsorption mechanisms. Many models of varied complexity have been developed to predict the uptake rate of the

adsorptive into the adsorbent [10,11]. Pseudo-first-order (PFO) and pseudo-second-order (PSO) models are the two most commonly used empirical models in liquid adsorption studies.

Most works focus on the novelty of the material. The kinetics studies in these works, in which experimental data are fitted to PFO and PSO models, serve merely to complement the adsorbent evaluation. Strong knowledge of the origins, strengths, and limitations of these models is sorely missing, as evident from these works. Little effort is made to investigate the underlying physico-chemical phenomena after the model fitting is completed. As such, the model parameters are merely empirical constants that have no distinct theoretical significance. Several works have attempted to rationalize these two empirical models and find the theoretical differences between them [12–15].

Ho [16] reviewed the applications of second-order models to adsorption systems. Liu and Liu [17] summarized the useful kinetic models for biosorption. Plazinski et al. [16] reviewed the adsorption kinetic models that had been theoretically associated with surface reaction mechanism. Batch and dynamic adsorption models were discussed by Alberti et al. [10]. However, these reviews were limited to selected models, and the discussion may have been overly complex for general or beginner readers. This review adopts a more general approach to reporting the major studies. It aims for a wider audience while retaining the essence of the kinetic studies.

The objective of this review is to promote better understanding of the kinetic modeling of liquid adsorption systems. While the focus is on batch adsorption, continuous fixed bed adsorption is discussed as well. Kinetic models relevant to aqueous adsorption

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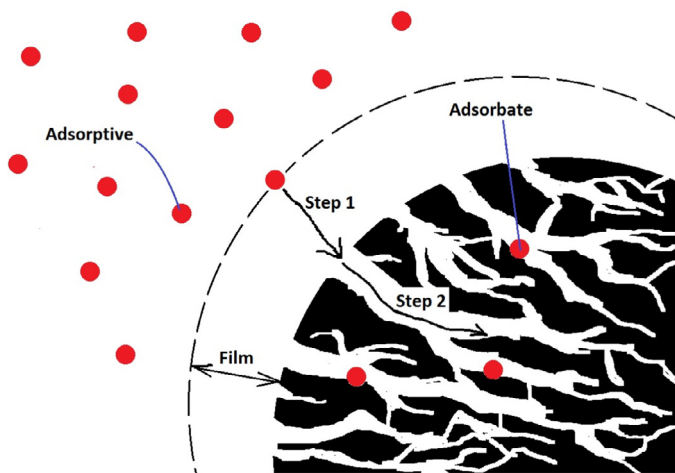 *E-mail address:* chbassim@usm.my (B.H. Hameed).

Fig. 1. Adsorption of an adsorptive molecule onto the internal surface of a porous adsorbent pellet. Step 1 is film diffusion, and Step 2 is pore diffusion.

kinetics in environmental remediation are presented. This paper also attempts to clarify ambiguities and doubts with regard to these models. The features and applicability of the models are discussed with reference to the literature. Theoretical origins or interpretations and modified versions of models are discussed where applicable.

The second objective is to highlight concerns in model discrimination. Issues arising from the selection of linear or nonlinear regression are brought to light. Certain widely used statistical error functions for regression and model comparison purposes are presented. This paper concludes with a summary of the modeling scenes of liquid adsorption kinetics, along with comments on the future of the field from the authors' perspective.

2. Principles of adsorption process

Adsorption is a surface phenomenon in which adsorptive (gas or liquid) molecules bind to a solid surface. However, in practice, adsorption is performed as an operation, either in batch or continuous mode, in a column packed with porous sorbents. Under such circumstances, mass transfer effects are inevitable. The complete course of adsorption includes mass transfer and comprises three steps [18]:

Step 1: Film diffusion (external diffusion), which is the transport of adsorptive from the bulk phase to the external surface of adsorbent.
Step 2: Pore diffusion [intraparticle diffusion (IPD)], which is the transport of adsorptive from the external surface into the pores.
Step 3: Surface reaction, which is the attachment of adsorptive to the internal surface of sorbent.

Fig. 1 depicts the trajectory of an adsorptive molecule during adsorption. The first two steps are transport steps, and the last step is a reaction step (Step 3, not labeled in Fig. 1). Each step presents a resistance to the adsorptive. The overall adsorption rate (as measured through an experiment) is determined by total resistance, which is the sum of the three component resistances in series [19]. The reduction of any component resistance increases the adsorption rate. The third step is typically very rapid compared with the first and second steps, and therefore poses negligible resistance. If one step contributes dominantly to the total resistance, to the point that reducing the other two resistances only marginally increases the adsorptive uptake rate, then the step is called a sole

rate-controlling step. The transport resistances depend on numerous factors, including adsorbent and adsorptive types, their properties, and operating conditions. The rate-controlling step can change during the adsorption process [20]. For dye adsorption on pine sawdust, the controlling mechanism switches from surface reaction to IPD when the adsorbent is 80% saturated [21].

Two types of interaction, namely, physical and chemical, are possible between adsorbent and adsorbate [22,23]; the former is known as physisorption, and the latter is chemisorption. Physisorption is a result of attractive forces between sorbent and adsorbate molecules [24], whereas chemisorption provides a stronger bond as it involves the transfer or sharing of electrons between adsorbent and adsorbate species. As a guideline, an isosteric heat of adsorption with magnitude between 5 and 40 kJ/mol indicates physisorption as the dominant adsorption mode, while one between 40 and 125 kJ/mol indicates chemisorption [25,26].

The monolayer capacity of an adsorbent is its capacity to accommodate a single layer of adsorbed species on the adsorbent surface. Often, when adsorptive concentration is high, because of intermolecular attraction, additional layers stack onto the first monolayer, thereby forming multilayer adsorption, which is physical in nature [22].

The heterogeneity of the adsorbent surface significantly affects adsorption equilibrium and kinetics. Heterogeneous adsorbents contain more than one type of adsorption site that can bind the adsorbate, and each site type has a different heat of adsorption. Surprisingly, Langmuir isotherm, which is based on homogeneous surface sites, can describe a large number of adsorption systems, many of which possess heterogeneous surface characteristics [27].

Adsorption study comprises two main aspects: equilibrium and kinetic studies. The attainment of equilibrium in adsorptive loading by the adsorbent is governed by thermodynamics. The rate of adsorptive uptake is dependent on the adsorption mechanism. The understanding of adsorption equilibrium has matured, as a wide variety of equilibrium isotherms exist for describing the equilibrium uptake of any target adsorptive. Conversely, adsorption kinetics theory is developing far more slowly despite its importance to practical applications of a given sorbent. The basis for kinetics study is the kinetic isotherm, which is obtained experimentally by tracking the adsorbed amount against time. Kinetic investigations develop a model to describe the adsorption rate. Ideally, the model should, with minimal complexity, (i) reveal the rate-limiting mechanism and (ii) extrapolate to operating conditions of interest. Accomplishing these two targets should enable one to identify operating conditions with minimal mass transfer resistance and predict adsorbent performance.

3. Modeling the kinetics of batch adsorption

3.1. Kinetic experiment

Adsorption kinetics can be represented by a plot of uptake vs. time; this plot is known as a kinetic isotherm. This plot forms the basis of all kinetics studies because its shape represents the underlying kinetics of the process. The kinetics are dependent on material factors, such as adsorbent and adsorbate types, and experimental factors, such as temperature and pH [28,29]. Typically, a batch experiment is conducted to collect kinetic data. Ensuring constant experimental conditions during batch adsorption is important.

The kinetic isotherm should ideally shed light on the intrinsic kinetics, which are the chemical kinetics on the adsorbent surface in the absence of transport limitations. Batch operation is an attractive method for studying intrinsic kinetics. Mass transfer effects are relatively easily reduced or eliminated by applying (i) high agitation speed (reduced film thickness) and (ii) small particle size (reduced pore diffusion resistance) [30].