Guidelines for general adsorption kinetics modeling

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TECHNICAL PAPER

UDC: 661.183+66.011

Hem. Ind. **74 (1)** 65-70 (2020)

Abstract

Adsorption processes are widely used in different technological areas and industry sectors, thus continuously attracting attention in the scientific research and publications. Design and scale-up of these processes are essentially based on the knowledge and understanding of the adsorption kinetics and mechanism. Adsorption kinetics is usually modeled by using several well-known models including the pseudo-first and pseudo-second order models, the Elovich equation, and the intra-particle diffusion based models. However, in the scientific literature there are a significant number of cases with the inappropriate use of these models, utilization of erroneous expressions, and incorrect interpretation of the obtained results. This paper is especially focused on applications of the pseudo-second order, intra-particle diffusion and the Weber-Morris models, which are illustrated with typical examples. Finally, general recommendations for selection of the appropriate kinetic model and model assumptions, data regression analysis, and evaluation and presentation of the obtained results are outlined.

Keywords: pseudo-second order kinetics; intra-particle diffusion; Weber-Morris model; linear regression; errors in kinetics modeling

1. INTRODUCTION

Adsorption is a common separation process widely used in many industrial applications such as wastewater treatment, purification of gases, heterogeneous catalysis, different chromatography techniques, etc. Due to the ease of operation, this process is constantly being explored with the stress on finding new low-cost, efficient and eco-friendly adsorbents. Thus, this topic is continuously attracting attention and it is in focus of many scientific studies. Modeling of adsoprtion/desorption kinetics is one of the main requirements for characterization of novel adsorbents and design of efficient adsorption processes. However, in the vast scientific literature on this topic, there are errors that are being propagated as we have previously pointed to [1] and as reviewed in literature [2]. Thus, the purpose of this paper is to provide guidelines for general adsorption kinetics modeling, in line with the requirements in the journal Hemijska industrija.

Kinetic models that are commonly used to describe adsorption processes from the liquid phase include the pseudo-first order (Lagergren's) model, the pseudo-second order model, the Elovich or Roginsky-Zeldovich model, the intra-particle diffusion model and the Weber-Morris model [2, 3]. Here, it should be noted that the adsorption process comprises several steps: transport of the adsorbate from the fluid bulk to the adsorbent surface (external mass transfer usually assumed by the film theory), transport of the adsorbate within the porous adsorbent (internal diffusion), and binding of the adsorbate to the adsorbent surface by a physical or chemical process. Thus, by applying the first three models it is assumed that the overall adsorption process rate is governed by the rate of binding, while by applying the last two models it is assumed that the rate of mass transport is governing the overall process rate. Consequently, only one of these two assumptions could be adopted or the process should be modeled by more complex models, which will include several or all steps in the adsorption process (*e.g.* [4]).

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Paper received: 01 February 2020
Paper accepted: 28 February 2020
https://doi.org/10.2298/HEMIND200201006O

It should be also added that the mentioned kinetic model equations describing the rate of adsorbate binding could be derived based on different reaction mechanisms assigning different meanings to the model parameters (*e.g*. [5]). Thus, when selecting the kinetic model, the adsorption mechanism should be closely inspected, while using the criterion "goodness of the fit" solely and without any scientific explanation has little significance [5].

Another issue is validity of the experimental adsorption data. For example, pH changes in the solution during the adsorption experiments are often neglected and not measured, while the solution pH significantly affects the adsorption kinetics and equilibrium values [2,5]. Also, the equilibrium is often assumed to be reached after a certain period of time without actually experimentally confirming the equilibrium attainment [2].

Correct equations for the kinetic models are summarized by Tran and coworkers [2] accompanied with commonly used erroneous forms. We would like here to emphasize the correct applications of the pseudo-second order, intra-particle diffusion and Weber-Morris models.

2. PSEUDO-SECOND ORDER MODEL

The pseudo-second order (PSO) model was first proposed by Blanchard and coworkers [6] and can be described by the equation:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k\left(q_\mathrm{e} - q\right)^2 \tag{1}$$

where q and q_e are the amounts of the adsorbate adsorbed per mass of the adsorbent at the time t and at the equilibrium, respectively, and k is the pseudo-second order rate constant. It should be noted that the model was originally proposed for the removal of divalent metal cations from water by using zeolites, while it could be also derived assuming additional adsorption/reaction mechanisms [7]. Integration of the eq. (1) yields:

$$q = \frac{{q_\mathrm{e}}^2 kt}{1 + q_\mathrm{e}kt} \tag{2}$$

The two model parameters, q_e and k, can be determined by the direct application of the eq. (2) to the experimental data by non-linear regression.

Additionally, in literature, four linear forms of the eq. (2) are used with the following one being the most frequent:

$$\frac{t}{q} = \frac{1}{k{q_\mathrm{e}}^2} + \frac{1}{q_\mathrm{e}}t \tag{3}$$

The model parameters are then determined by the best linear fit of the experimental data plotted as t/q *vs*. t. Although this method can also lead to acceptable results, it should be kept in mind that it is a spurious correlation [8]. Since the variable t appears on both sides of the eq. (3) it leads to a better linear correlation. In specific, the initial data center near the origin while data at later times, near the equilibrium, carry more weight in the regression [8].

The weaknesses of such a correlation are visible when the model predictions are plotted with the experimental data in the non-linear form (*i.e*. as the adsorbed amount *vs*. time). Also, calculations of coefficients of determination (R^2) for the model in linear and nonlinear forms can quantitatively show the difference [8]. This case can be illustrated by an example of experimental data of adsorption of a contaminant, where the last measured point deviates from a trend indicated by the initial data points (Fig. 1a). Application of the linear form of the PSO model (eq. 3) yields seemingly excellent model agreement (Fig. 1c) with the coefficient of determination of $R^2 = 0.994$. However, when the model predictions are plotted together with the experimentally determined amounts of adsorbed contaminant over time, it is clearly visible that the last experimental point largely affected the regression outcome (Fig. 1a,b). Accordingly, the coefficient of determination decreased to $R^2 = 0.884$. On the other hand, non-linear regression that is direct application of the eq. (2) to the experimental data, took into account all experimental values and predicted better the initial adsorption (Fig. 1b) with a higher overall coefficient of determination ($R^2 = 0.910$).

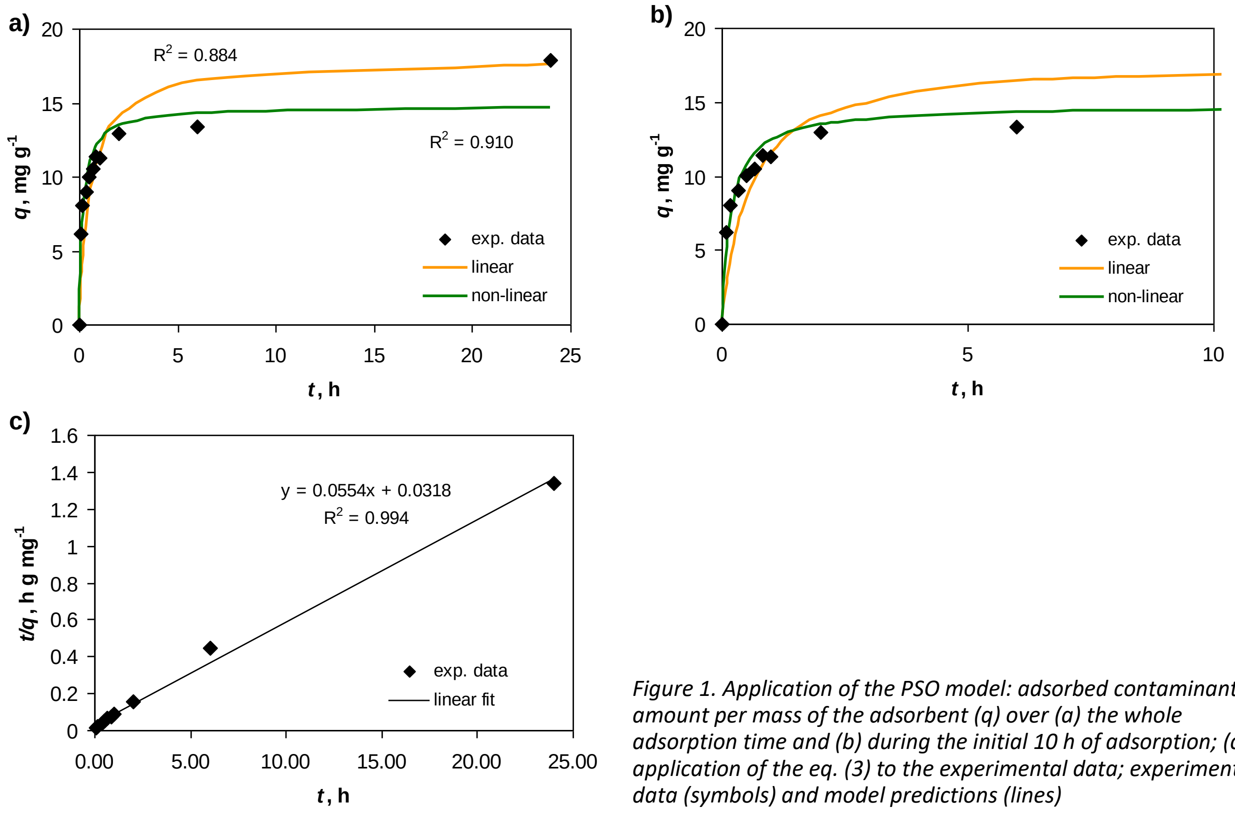

Figure 1. Application of the PSO model: adsorbed contaminant amount per mass of the adsorbent (q) over (a) the whole adsorption time and (b) during the initial 10 h of adsorption; (c) application of the eq. (3) to the experimental data; experimental data (symbols) and model predictions (lines)

The two regression methods also yielded significantly different values of model parameters (Table 1). In the real situation the last experimental point would be certainly validated in additional experiments in order to determine the best kinetic model. However, this example clearly shows how the application of the PSO model in the linear form may lead to erroneous conclusions.

Table 1. Values of the PSO model parameters q_e *and k obtained by linear and non-linear regression analyses of the experimental data presented in Figure 1*

	q_e / mg g^{-1}	k / g mg^{-1} h^{-1}
Linear regression	18.0	0.10
Non-linear regression	14.8	0.35

3. INTRA-PARTICLE DIFFUSION MODEL

The intra-particle diffusion model is based on the solution of the Fick's second law of diffusion approximated for short times. The exact and approximated solutions for different times and geometries can be found in the review of Siepmann and Siepmann [9]. In adsorption studies, usually the adsorbent particles are assumed to be spherical leading to the expression for the initial times ($q/q_e < 0.4$):

$$\frac{q}{q_e} = \frac{6}{R}\sqrt{\frac{Dt}{\pi}} \tag{4}$$

where R is the radius of the spherical particle and D is the apparent diffusion coefficient of the adsorbate within the particle to the binding site that may include several processes such as diffusion through the pores, surface diffusion, etc. The intra-particle diffusion model is usually applied to the experimental data in the simplified form:

$$q = k_p\sqrt{t} \tag{5}$$

where k_p is the rate constant determined by linear regression of the experimental data plotted as q *vs.* $t^{0.5}$. The apparent diffusion coefficient D is then calculated from the rate constant. In order for this model to be applicable, the plot should pass through the origin and follow a linear trend up to the time when 40 % of the equilibrium amount is adsorbed ($q/q_e < 0.4$).

It should be noted that some literature reports propose multiple linear regressions apparently indicating different phases in the adsorbate mass transport from the bulk liquid to the binding site [2]. However, this would imply that the rate controlling steps are changing over time, which is usually not supported by the experimental settings and the quantity and quality of experimental data. Thus, multiple linear regressions usually do not show meaning in adsorption studies and just show that the intra-particle diffusion model is not appropriate.

4. WEBER-MORRIS MODEL

The Weber-Morris model [10] is based on the intra-particle diffusion model with the addition of a constant (C) that is related to a resistance (usually assumed as the mass transfer resistance in the liquid boundary layer), which delays the adsorption:

$$q = k_p \sqrt{t} + C \tag{6}$$

Thus, it should be noted that the constant C has to be negative value. An example is illustrated in Figure 2. The whole experimental time lasted for 24 h while the model was applied to the first 6 experimental points (without the initial (0,0) point) for which the condition $q/q_e < 0.4$ was fulfilled (Fig. 2c). The experimental data yielded a straight line with a negative interception with the ordinate (C = -2.43 mg g^{-1}) and a positive interception with the abscise yielding a lag time of t_{lag} = 0.03 h. Thus, the adsorption process was delayed for approximately 1.8 min due to the external mass transfer resistance or some other process.

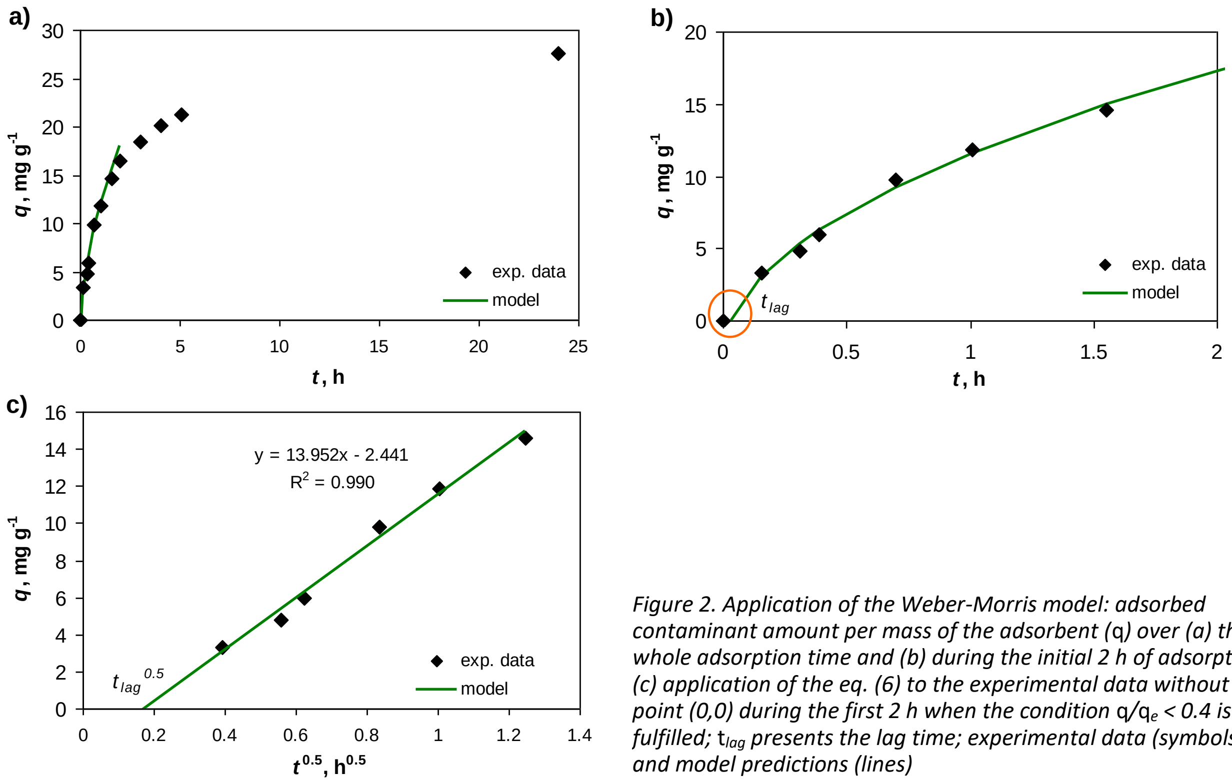

Figure 2. Application of the Weber-Morris model: adsorbed contaminant amount per mass of the adsorbent (q) *over (a) the whole adsorption time and (b) during the initial 2 h of adsorption; (c) application of the eq. (6) to the experimental data without the point (0,0) during the first 2 h when the condition* $q/q_e < 0.4$ *is fulfilled;* t_{lag} *presents the lag time; experimental data (symbols) and model predictions (lines)*

A positive intercept with the ordinate (*i.e.* $C > 0$) would mean that some amount of the adsorbate is already adsorbed at the initial point at t = 0. In studies of drug release kinetics from reservoirs, such result would indicate a burst release corresponding to a higher release rate at initial times than the steady state release rate by diffusion [9]. In the case of adsorption, such result would probably indicate that the Weber-Morris model is not appropriate.

4. CONCLUSION

Description of adsorption kinetics is commonly based on application of several well-known models, such as pseudo-first and pseudo-second kinetic models as well as the intra-particle diffusion model. Still, care should be taken when choosing the correct model, assuming the rate controlling step, and analyzing the modeling results. Theoretical bases of the models and approximations should be kept in mind, and the original works should be referenced with the use of correct expressions. Special attention should be put on spurious correlations and non-linear regression analysis is recommended. Kinetic modeling results should be always plotted along with the experimental data in the non-linear form and appropriateness of the model should be inspected throughout the whole adsorption period. The commonly used intra-particle diffusion equation is an approximation for early adsorption times while the Weber-Morris model should be applied only in the case of a delayed adsorption process. Finally, all mentioned models simplify the adsorption process to only one rate-controlling phase and may not be appropriate for describing certain experimental results. In such cases, development of more complex kinetic models based on the process mechanism is needed.

Acknowledgements: *This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (grant III45019).*

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SAŽETAK

Smernice za uobičajeno modelovanje kinetike adsorpcije

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(Stručni rad)

Procesi zasnovani na adsorpciji su široko korišćeni u različitim tehnološkim oblastima i industrijskim sektorima tako da kontinualno privlače pažnju u naučnim istraživanjima i publikacijama. Dizajn i uvećanje razmera tih procesa su u suštini zasnovani na poznavanju i razumevanju kinetike i mehanizma adsorpcije. Kinetika adsorpcije je uobičajeno modelovana primenom nekoliko opštepoznatih modela uključujući modele pseudo-prvog i pseudo-drugog reda, Elovičev model i modele zasnovane na unutrašnjoj difuziji. Međutim, u naučnoj literaturi se može naći značajan broj radova sa neprikladnom primenom tih modela, primenom pogrešnih jednačina i netačnom interpretacijom dobijenih rezultata. Ovaj rad je posebno fokusiran na primenu modela kinetike pseudo-drugog reda, zatim modela unutrašnje difuzije i Veber-Morisovog (Weber-Morris) modela koji su ilustrovani tipičnim primerima. Najzad, date su opšte preporuke za izbor odgovarajućeg kinetičkog modela i polaznih pretpostavki, primenu regresione analize, kao i za ocenu i prikaz dobijenih rezultata.

Ključne reči: kinetika pseudo-drugog order reda; model unutrašnje difuzije; Veber-Morisov model; linearna regresija; greške u modelovanju kinetike