

# A New Film Diffusion Controlling Kinetic Model for Adsorption at the Solid/Solution Interface

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**ABSTRACT:** A convenient adsorption kinetic equation has been offered for the modeling of adsorption kinetics in batch systems when diffusion taking parts to the rate-controlling step of adsorption. This model is suggested based on the Smoluchowski-Waite equation for diffusion-controlled second-order reactions. The proposed new model has better performance (lower absolute values of the relative errors (AARE) %) respect to the pseudo-second-order. Results of this equation are in agreement with experiment data especially at the initial times of adsorption that diffusion contributes to the rate-controlling step of adsorption.

**KEYWORDS:** Adsorption; Kinetics; Film diffusion.

## INTRODUCTION

sorption as treatment approach, is an effective separation and economic technique that has been widely considered from kinetic and equilibrium aspects [1-2]. The adsorption of an adsorbate from a liquid solution generally can be divided into three steps [3, 4]: (1) transport of solute across the liquid film circumambient the adsorbent particle (external film diffusion); (2) diffusion of solute within the pore adsorbent particle (intraparticle diffusion); (3) adsorption on the solid surface (surface reaction).

It is needed to explain accurately the kinetics of adsorption to compare the calculated adsorption parameters obtained by models to the experimental adsorbent behavior [5]. Variety models have been introduced for describing kinetic of adsorption in the solid solution interface. For example, Elovich [6], Langmuir [7], statistical rate theory [8], intraparticle diffusion model [9], pseudo first-order(PFO)and pseudo

Second-order (PSO) [10] are the most important sorption kinetic models. The other adsorption rate equations such as exponential kinetic model [11], hyperbolic tangent model [12], Mixed Surface Reaction and Diffusion Kinetic Model [13], modified pseudo first-order [14], modified pseudo second-order [15], pseudo n- order [16], modified pseudo n-order [17], two-site pseudo second-order [18], mixed 1,2-order equation [19] have been introduced to illustrate kinetic data for adsorption batch processes. And also already, Yao [20] proposed a new developed linear regression approach where the main kinetic equations are maintained without transformation.

At the initial times of adsorption that external film diffusion is important; the mentioned models do not describe the kinetic data very accurately. So the aim of this study is to introduce a convenient kinetic equation that the effects of the present of diffusion and surface reaction have been taken into account together with

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to Evaluate the kinetics of adsorption. Ten adsorption systems are chosen to illustrate the application of the model. Results of this model are in agreement with experiment data.

### Theory

Despite the variety of kinetic models, it seems that PFO, intraparticle diffusion equation, and particularly PSO models are still the most common and popular kinetic equations

### Pseudo First Order Equation (PFO)

The PFO model can illustrate the kinetics of sorption when comparative surface coverage during the process is negligible. The PFO has written as bellows [21]:

$$\frac{dq}{dt} = k_1 (q_e - q) \quad (1)$$

Where  $k_1$  is the pseudo first order rate coefficient,  $q_e$  and  $q$  are the amounts of the adsorbed species per unit mass of adsorbent at the equilibrium state and any time of adsorption, respectively.

### Pseudo-Second-Order Equation (PSO).

PSO equation is the most common equation for modeling of the adsorption kinetic data. The differential expression of this model has as follow form [10]:

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

Where  $k_2$  is the PSO rate coefficient. Real form of the above equation is expressed as

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

The most popular linear forms PSO model is written as follows:

$$\frac{t}{q} = \left( \frac{1}{k_2 q_e^2} \right) + \left( \frac{1}{q_e} \right) t \quad (4)$$

### Intraparticle Diffusion Model (IDM).

For intraparticle diffusion controlled adsorption in spherical adsorbents, the following series expression is presented by *Boyd et al.* in 1947[22].

$$\frac{q}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_{int} n^2 \pi^2 t}{r^2}\right) \quad (5)$$

Where  $D_{int}$  is the intraparticle diffusion coefficient and  $r$  is the particle radius. For short times, Eq.(5) can be approximated by

$$q = k_{ID} \sqrt{t} \quad (6)$$

Where  $k_{ID}$  is constant of the intraparticle diffusion. Linear plot of  $q$  vs  $\sqrt{t}$  cross through the origin shows that the intraparticle diffusion is the only rate-controlling step.

### Description of a new model

Based on the *Smoluchowski* equation [23] which it has been explained the rate of the process at any time is that the single reactants diffuse together multiplied by the number of A and B present in bulk at any time:

$$\frac{dC_A}{dt} = \frac{dC_B}{dt} = -k' \left( 1 + \frac{\tau^{0.5}}{t^{0.5}} \right) C_A C \quad (7)$$

Where

$$\tau = \frac{r_o^2}{\pi D} \quad (8)$$

In which  $r_o$  is radius of the reaction cage,  $k'$  is  $4\pi r_o (D_A + D_B)$ ,  $C_A$  and  $C_B$  are concentrations of A and B, respectively,  $t$  is time and  $D$  is the diffusion coefficient from the bulk solution to the interface. For adsorption processes at the solid/solution interface, we take into account that the adsorbate species diffuse to the adsorbent sites and then adhere on the surface positions. So, two rectifications are considered in Eqs. (7) and (8). The first one is A and B is considered adsorbate and adsorbent. The second modification, instead of bulk concentration B ( $C_B$ ), we assume that the value of existing vacant positions on the adsorbent at given time

Table 1: The reported details of Experimental data used in this research.

Sys. no.	Data	Reference
1	Azocarmine B adsorption onto P-g-pAPTAC microspheres	[24]
2	Neutral Red adsorption on peanut husk	[25]
3	food yellow 3 on chitosan	[26]
4	cadmium(II) ions on eucalyptus bark	[27]
5	Pb(II) ion on clinoptilolite	[28]
6	Dye removal on activated carbon	[29]
7	Acid violet 17 on Orange peel	[30]
8	Malachite Green on cyclodextrin	[31]
9	organic chloride on Na-LSX zeolite	[32]
10	naproxen onto functionalized nano-clay	[33]

and concentration, which is equivalent to  $(q_e - q)^2$ . Then, by taking account the mentioned rectifications, one derives

$$\frac{dC}{dt} = -k' \left( 1 + \frac{\tau^{0.5}}{t^{0.5}} \right) C (q_e - q)^2 \quad (9)$$

Where  $C$  is the concentration of adsorbate in the bulk of liquid at each time. The adsorbate concentration in bulk ( $C$ ) is diminished though of adsorption operation, so  $C$  at any time is written as follows

$$C = C_0 - \frac{(C_0 - C_e)q}{q_e} \quad (10)$$

By replacing Eq. (10) in Eq. (9) make the following equation

$$\frac{dq}{dt} k \left( 1 + \frac{\tau^{0.5}}{t^{0.5}} \right) \left( C_0 - \frac{(C_0 - C_e)q}{q_e} \right) (q_e - q)^2 \quad (11)$$

$$\text{where } k = \frac{k'q_e}{(C_0 - C_e)}$$

After integration, we have

$$\frac{\left( 1 - \frac{C_0}{C_e} \right)}{q_e} \ln \left( \frac{1 - \frac{q}{q_e}}{1 - \left( 1 - \frac{C_e}{C_0} \right) \frac{q}{q_e}} \right) + \frac{1}{q - q_e} + \frac{1}{q_e} = \quad (12)$$

$$At + Bt^{0.5}$$

Where

$$A = kC_e \quad \text{an} \quad B = 2kC_e\tau^{0.5} \quad (13)$$

Equation (12) is the new model taking account both diffusion and surface reaction as the rate-limiting stages

## RESULTS AND DISCUSSION

In order to evaluate the proposed model compare with PSO for modeling of adsorption kinetics at the solid/solution interface, the available data of adsorption had been collected from the literatures. Table 1 shows 10 systems. The arithmetic average of the absolute values of the relative errors (AARE) was determined to provide an indication of the accuracy of the correlation. The AARE can be written as:

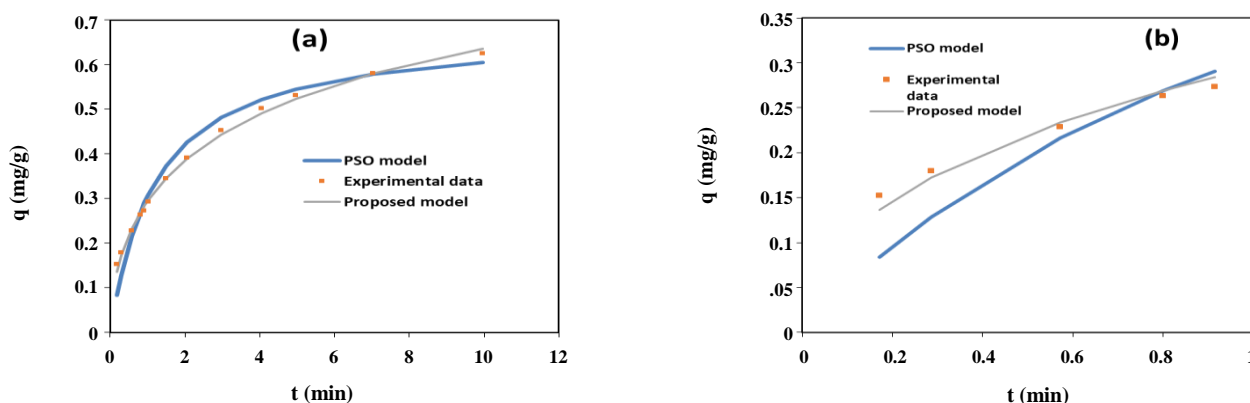
$$\text{AARE}\% = \frac{100}{N} \sum_{i=1}^N \left| \frac{q^{\text{exp}} - q^{\text{cal}}}{q^{\text{exp}}} \right| \quad (14)$$

In this equation,  $N$  is the number of data points,  $q^{\text{exp}}$  is the experimental amount of the adsorbed species per unit mass of adsorbent at any time of adsorption and  $q^{\text{cal}}$  is the calculated one.

Table 2 represented AAREs for all data sets produced by the proposed model and the PSO model. As mentioned earlier, in most of the articles the linear format PSO equation is the extensively applied equation for modeling of adsorption kinetics. Results disclosed that the suggested model was more accurate compared

**Table 2: AARE (%) for 10 experimental data sets produced by proposed model and pseudo second kinetic model.**

Sys. no.	Proposed model	pseudo second kinetic model
1	2.52	9.79
2	3.04	16.15
3	1.06	7.03
4	0.69	2.0
5	2.19	7.85
6	1.81	3.31
7	2.0	2.34
8	4.40	5.88
9	3.39	5.84
10	0.85	1.25
Mean	2.19	6.14

**Fig. 1: Variation of  $q$  with time: (a): total time (b) initial time.**

with the PSO model. The mean AARE% values for the PSO is 6.14, whereas the mean AARE% values for the suggested model is 2.19.

Fig. 1a represents the Changes of  $q$  with time for dates [19] according to on new model and PSO model. This figure presents that  $q$  Changes with time by Eq 12 is very accommodation to the experimental one. Fig. 1b shows the variation of  $q$  with time for the initial time that diffusion effects the rate-controlling step of adsorption, the rustles express that the new equation is in agreement with data in compared to PSO model.

In another report the adsorption of food yellow 3 onto chitosan was considered [25]. Fig. 2a shows the variation

of  $q$  with time for this data based on new equation and PSO model. Fig. 2b represents the variation of  $q$  with time for initial time. In both Figures, the proposed model is better than the PSO model.

## CONCLUSIONS

In this research, a new kinetic equation was introduced that effect of existence of diffusion and surface reactions on adsorption kinetics at the solid/solution interface in batch experimental data is considered. Accuracy of the model was compared with PSO model using 10 published adsorption data sets. The results showed the new model has excellent agreement

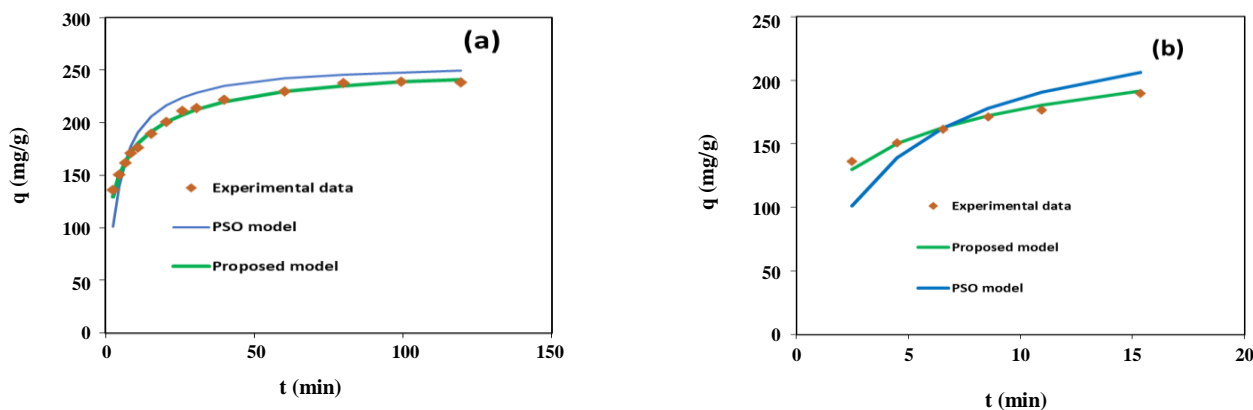


Fig. 2: Variation of  $q$  with time: (a): total time (b) initial time.

with those reported in the literature especially at initial times of adsorption.

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