Short communication

Pseudo second order kinetic models for safranin onto rice husk: Comparison of linear and non-linear regression analysis

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Abstract

Kinetic experiments were carried out for the sorption of safranin onto rice husk particles. The kinetic data were fitted to pseudo second order model of Ho, Sobkowsk and Czerwinski, Blanachard and Ritchie by linear and non-linear regression method. Non-linear method was found to be a better way of obtaining the parameters involved in the second order rate kinetic expressions. Both linear and non-linear regression showed that the Sobkowsk and Czerwinski and Ritchie's pseudo second order model were the same. Non-linear regression analysis showed that both Blanachard and Ho have similar ideas on the pseudo second order model but with different assumptions. The best fit of experimental data in Ho's pseudo second order expression by linear and non-linear regression method showed that Ho pseudo second order model was a better kinetic expression when compared to other pseudo second order kinetic expressions.
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1. Introduction

Adsorption process is proved to be an effective process for the removal of various pollutants from its aqueous solutions. The prediction of batch kinetics is necessary for the design of sorption systems. Chemical kinetics explain how fast the rate of chemical reaction occurs and also on the factors affecting the reaction rate. The nature of sorption process will depend on physical or chemical characteristics of the adsorbent system and also on the system conditions. Previously several researchers used different kinetic models to predict the mechanism involved in the sorption process. Kinetics model based on the concentration of solute and also on the concentration of sorbent have been proposed by several researchers. The kinetic models based on the solute concentration include the first order [1], second order [1], reversible first order kinetics [2]. The kinetic models based on the sorbent concentration include the Lagergren pseudo first order [3], Ritchie second order [4], Sobkowsk and Czerwiński second order [5], Blanachard et al. second order [6] and Ho and McKay

[7] pseudo second order kinetics. In addition, mechanism based kinetic expressions were also proposed by several researchers. The solute concentration based mechanism involving kinetics are the external mass transfer model of Furusawa and Smith [8], Weber and Morris intraparticle diffusion model [9] and Boyd's pore diffusion kinetics [10]. Multiple first order kinetics using the Lagergren's equations was previously reported by Sarkar and Chattoraj [11] for protein/silica sorption system. Though several kinetic models are available in literature, except Ho's pseudo second order model, no other model represents well the experimental kinetic data for the entire sorption period for most of the systems. The excellent fit of experimental kinetic data for the entire sorption period makes this model be widely used by several researchers to represent various sorbate/sorbent systems. A review on the applicability of the Ho pseudo second order kinetic model to various sorption systems was made earlier [12]. However careful literature analysis showed that several researchers had different approaches in obtaining the pseudo second order expression for sorption systems. In 1977, Ritchie [4] proposed a second order expression as an alternate to Elovich kinetics for gaseous systems assuming that the rate of adsorption depends solely on the fraction of sites unoccupied at any time t. The author assumes that $\theta = q/q_e$ is the fraction of surface sites that are occupied by an adsorbed gas, k

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(min^{-1}) is the rate constant. Assuming the rate of adsorption depends solely on the fraction of sites unoccupied at time t, the rate of a reaction can be expressed as:

$$\frac{d\theta}{dt} = k(1-\theta)^n \tag{1}$$

where n represents the order of the reaction. At time $t = 0$, it is assumed that no site is occupied. Introducing the term, amount of dye adsorbed, q (mg/g) at time t (min), and the amount of dye adsorbed at equilibrium, q_e (mg/g), the integrated form of Eq. (1), for $n = 2$ becomes:

$$\frac{q_e}{q_e - q} = kt + 1 \tag{2}$$

Thus, the rate constant k can be obtained from the plot of $q_e/(q_e - q)$ versus time t.

Previously Sobkowsk and Czerwiński [5] proposed first and second order kinetic expression similar to that of Ritchie's expression for CO_2 adsorption onto a platinum electrode based on the maximum uptake capacity of the sorbents. Sobkowsk and Czerwiński concluded that first order process can be applied for the lower surface concentrations of solid and the second order for higher surface concentrations. The second order kinetic expression of Sobkowsk and Czerwiński is given by:

$$\frac{\theta}{1-\theta} = kt \tag{3}$$

where $\theta = q/q_e$, is the fraction of surface sites that are occupied by an adsorbed gas or solute particles. The second order rate constant k (min^{-1}) can be evaluated from the plot of $\theta/(1-\theta)$ versus time t.

In 1984, Blanachard et al. proposed [6] a second order rate equation similar to that of Ritchie's model for the exchange reaction of divalent metallic ions onto NH_4^+ ions fixed zeolite particles. The linearized form of Blanachard's second order kinetics was given by:

$$\frac{1}{q_e - q} - \alpha = kt \tag{4}$$

Thus the rate constant k (g/mg min), can be obtained from the slope of plot between $1/(q_e - q)$ versus time t. Applying boundary conditions $q = 0$ for $t = 0$, it follows that $\alpha = 1/q_e$. Thus this model has an advantage to predict the equilibrium uptake capacity without the support of experimental data.

Recently, Ho and Mckay [7] proposed a second order model for the sorption of divalent metal ions onto peat particles based on the sorption capacity of adsorbents. In order to differentiate the kinetics of second order rate expressions based on the sorbent concentration from the models based on solute concentration, Ho and Mckay mentioned as pseudo second order rate expression [7]. The sorption kinetics following pseudo second order model as given by Ho is given by:

$$\frac{dq}{dt} = k(q_e - q)^2 \tag{5}$$

where q and q_e represents the amount of dye adsorbed at any time t(mg/g), k is the rate of sorption (g/mg min) and q_e is the amount of dye adsorbed onto activated carbon at equilibrium (mg/g).

Separating Eq. (5), gives:

$$\frac{dq}{(q_e - q)^2} = k\,dt \tag{6}$$

Let the term $(q_e - q) = X$ in Eq. (6), then

$$q_e - q = X \tag{7}$$

$$-dq = dX \tag{8}$$

Based on Eqs. (7) and (8), the rate Eq. (6) can be simplified as

$$-\frac{dX}{X^2} = k\,dt \tag{9}$$

Substituting the boundary conditions $q = 0$ at $t = 0$ and $q = q$ at $t = t$, the new boundary conditions for the Eq. (8) can be obtained as follows:

$$t = t, \qquad X = q_e$$

and

$$t = 0, \qquad X = q_e - q$$

Integrating the Eq. (9) with respect to the new boundary conditions, Eq. (9) becomes

$$\frac{1}{q_e - q} = \frac{1}{q_e} + kt \tag{10}$$

Eq. (10) was reported by Ho to explain the sorption kinetics of divalent metal ions onto peat particles assuming chemisorption. Previously, a similar expression was reported by Blanachard et al. [6] to explain the kinetics of exchange reaction of divalent metallic ions onto NH_4^+ ions fixed zeolite particles

Eq. (10) can be further linearized to [7]:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{11}$$

In the present study, all the four different types of pseudo second order expressions were used to represent the kinetics of safranin onto rice husk particles. Also a comparison of linear and non-linear method was made to predict the optimum sorption kinetics and also to obtain the kinetic parameters.

2. Experimental

The solute used in all the experiments was safranin, a basic (cationic) dye. The structure of safranin (CI: basic red 2) is given by: