

Short communication

Pseudo-second order models for the adsorption of safranin onto activated carbon: Comparison of linear and non-linear regression methods

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Abstract

Kinetic experiments were carried out for the sorption of safranin onto activated carbon particles. The kinetic data were fitted to pseudo-second order model of Ho, Sobkowsk and Czerwinski, Blanchard et al. and Ritchie by linear and non-linear regression methods. 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 models were the same. Non-linear regression analysis showed that both Blanchard et al. 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. Previously several researchers used different kinetic models to predict the mechanism involved in the sorption process. These kinetics models can be either based on the concentration of solute or such as the first order [1], second order [1], reversible first order kinetics [2] or kinetic models based on the sorbent concentration such as Lagergren pseudo-first order [3], Ritchie second order [4], Sobkowsk and Czerwiński second order [5], Blanchard et al. second order [6] and Ho and McKay [7] pseudo-second order kinetics. 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 [8]. However careful literature analysis showed that several researchers had proposed pseudo-second order kinetic models for different systems with different approaches. These include the models proposed by Ritchie [4], Sobkowsk and Czerwiński [5] and Blanchard et al. [6]. The Ritchie model assumes that the rate of adsorption depends solely on the fraction of sites, θ , unoccupied at time t . Previously Sobkowsk and Czerwiński [5] proposed a first and second order kinetic expression similar to that of Ritchie's expression for CO₂ 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. Later in 1984, Blanchard et al. proposed [6] a second order rate equation for the exchange reaction of divalent metallic ions onto NH₄⁺ ions fixed zeolite particles. In recent year Ho and McKay [7] reported the second order kinetics for the sorption of divalent metal ions onto peat particles. The models of Blanchard et al. [6] and Ho and McKay [7] had an advantage to predict the equilibrium uptake capacity without the support of extensive experimental kinetic data. In order to differentiate the kinetics of second order rate expressions based on the sorbent concentration from the models based

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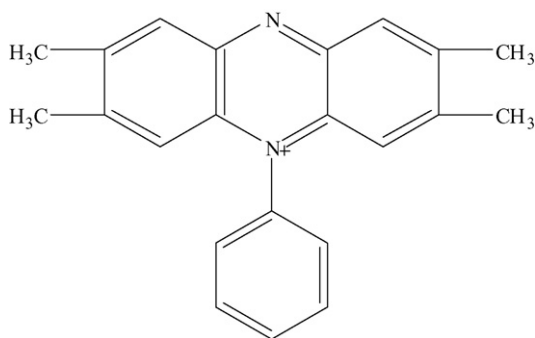
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on solute concentration, Ho used the term as pseudo-second order rate expression [7].

In the present study, all the four different types of pseudo-second order expressions were used to represent the kinetics of safranin onto activated carbon. Also a comparison of linear and non-linear regression method was made to predict the optimum sorption kinetics and also to obtain the kinetic parameters. Safranin/activated carbon system as a model system in order to analyze different pseudo-second order kinetic expressions proposed by several researchers.

2. Experimental

The solute used in all the experiments was safranin, a basic (cationic) dye. Synthetic dye solutions were prepared by dissolving weighed amount of safranin in one liter of double distilled water. The structure of safranin (CI: Basic Red 2) is given by



The stock solution of safranin was prepared by dissolving one gram of safranin in 1 l of distilled water. All working solutions were prepared by diluting the stock solution with distilled water.

The powdered activated carbon used in the present study was obtained from E-Merck Limited, Mumbai. The obtained activated carbon was directly used as adsorbents without any pretreatment. Some of the specifications of the activated carbon used in the present study as supplied by the manufacturer are given by: substances soluble in water $\leq 1\%$, substances soluble in HCl $\leq 3\%$, Cl $\leq 0.2\%$, and $\text{SO}_4^{2-} \leq 0.2\%$. Heavy metals as lead (Pb) $\leq 0.005\%$, Iron (Fe) $\leq 0.1\%$, and incomplete carbonization: passes test, methylene blue adsorption $< 180 \text{ mg/g}$, loss on drying $\leq 10\%$, and residue on ignition $< 5\%$.

Sorption kinetics experiments were carried out using mechanically agitated overhead laboratory stirrers. The effect of dye concentration on the adsorption rate were estimated by agitating 1.5 L of dye solution of known initial dye concentration with 0.3 g of activated carbon in 2 L beakers at room temperature (32°C) at a solution pH of 8 and at a constant agitation speed of 800 RPM. 2.5 mL of samples were pipetted out using 10 mL syringe filter at different time intervals. The collected samples were then centrifuged and the concentration in the supernatant solution was analyzed using UV spectrophotometer at a maximum absorbance wavelength of 530 nm.

3. Results and discussions

In the present study the best fit of a kinetic expression to the experimental data was tested using the value of coefficient of

Table 1
Linearized forms of second-order models

Author	Linear form	Plot
Sobkowsk and Czerwiński [5]	$\frac{\theta}{1-\theta} = kt$	$\frac{\theta}{1-\theta}$ vs. t
Ritchie [4]	$\frac{q_e}{q_e - q} = kt + 1$	$\frac{q_e}{q_e - q}$ vs. t
Blanchard et al. [6]	$\frac{1}{q_e - q} - \alpha = kt$, where $\alpha = \frac{1}{q_e}$	$\frac{1}{q_e - q}$ vs. t
Ho and McKay [7]	$\frac{t}{q} = \frac{1}{kq_e^2} + \frac{t}{q_e}$	$\frac{t}{q}$ vs. t

determination, r^2 , which is defined as

$$r^2 = \frac{\sum (q_{\text{predicted}} - \bar{q}_{\text{experimental}})^2}{\sum (q_{\text{predicted}} - \bar{q}_{\text{experimental}})^2 + \sum (q_{\text{predicted}} - q_{\text{experimental}})^2} \quad (1)$$

Linear regression was the most commonly used method to obtain the parameters involved in the kinetic expression and also in predicting the best-fit kinetic expression. The linearized forms of the different pseudo-second order kinetic expressions were shown in Table 1. The kinetic parameters involved in the Ritchie [4], Sobkowsk and Czerwiński [5], Blanchard et al. [6] and Ho and McKay [7] pseudo-second order models were obtained from the plots between $q_e/q_e - q$ versus t , $\theta/1 - \theta$ versus t , $1/q_e - q$ versus time t , respectively. The ways to obtain the kinetic parameters were shown in Table 1. The calculated kinetic rate constants and their corresponding coefficient of determinations r^2 were given in Table 2. Table 2 also shows the experimental q_e value at different initial dye concentrations. From the Table 2, it was observed that except Ho pseudo-second order expression, no other model provide a better fit to the experimental kinetic data. In addition the Blanchard et al. expression which has advantage to predict the q_e without knowing the experimental details fails to predict the correct q_e values. This showed that Ho's pseudo-second order kinetic expression is the best-fit second order kinetic expression that represents well the kinetics of adsorption of safranin onto activated carbon for the entire sorption period.

The kinetic parameters involved in the four-pseudo-second order models were further estimated using non-linear method. For non-linear regression method, a trial and error procedure, which is applicable to computer operation, was used to determine the kinetic parameters by maximizing the respective the coefficient of determination between experimental data and kinetics using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel. The non-linearized form of the four types of second order models were shown in Table 3. From Table 3 it was observed that the second order models of Ritchie and Sobkowsk and Czerwiński's transforms to a similar non-linear expression. This suggests that both Ritchie and Sobkowsk and Czerwiński have the same idea on pseudo-second order expression. Likewise the second order expressions of Blanchard et al. and Ho transforms to a same non-linear expression. This shows that Blanchard et al. and Ho have similar idea on the pseudo-second order expression. However Blanchard et al. proposed their model for an ion exchange mechanism, whereas Ho's pseudo-second order

Table 2
Kinetic constants for safranin onto activated carbon particle by linear and non-linear regression analysis method

Co (mg/L)	q_e , experimental	Ritchie		Sobkowsk and Czerwiński		Blanchard		Ho					
		k (min^{-1})	r^2	k (min^{-1})	r^2	k (g/mg min)	α (g/mg)	q_e , predicted (mg/g)	r^2	k (g/mg min)	q_e , predicted	h (mg/g min^0)	r^2
Linear regression method													
10	256	0.689888	0.79339	0.689888	0.79339	0.002695	-0.00646	-154.904	0.79339	0.00103	266.3309	73.09119	0.999432
20	388	0.761673	0.862787	0.761673	0.862787	0.001963	-0.00393	-254.557	0.862787	0.001115	396.2082	175.0606	0.999784
30	508	1.302403	0.939278	1.302403	0.939278	0.002564	-0.00328	-304.742	0.939278	0.001535	514.3154	405.9359	0.999943
40	615	1.724928	0.830188	1.724928	0.830188	0.002805	-0.00731	-136.86	0.830188	0.001511	621.8713	584.3601	0.999908
50	676	1.674541	0.889098	1.674541	0.889098	0.002477	-0.00283	-353.547	0.889098	0.001749	682.3738	814.5006	0.999934
Non-linear regression													
10	256	0.301207	0.988438	0.301207	0.988438	0.00097	0.003738	267.5443	0.994965	0.00097	267.5421	69.40773	0.994965
20	388	0.536869	0.995656	0.536869	0.995656	0.001371	0.002573	388.7219	0.995673	0.001371	388.7033	207.1964	0.995673
30	508	0.922797	0.995087	0.922797	0.995087	0.001806	0.001966	508.5353	0.995094	0.001806	508.5267	466.9867	0.995094
40	615	1.293782	0.986054	1.293782	0.986054	0.002267	0.001644	608.0946	0.986997	0.002266	608.1072	838.1217	0.986997
50	676	2.819728	0.924003	2.819728	0.924003	0.002439	0.001491	670.6447	0.988847	0.002438	670.6721	1096.695	0.988847

^a h is the initial sorption rate [7] and is given by $h = kq_e$.

Table 3
Non-linear form of pseudo-second order kinetic expressions

Kinetics	Non-linear form	Reference
Sobkowsk and Czerwinski	$q = \frac{q_e kt}{kt+1}$	[5]
Ritchie	$q = \frac{q_e kt}{kt+1}$	[4]
Blanchard	$q = \frac{ktq_e + \alpha q_e - 1}{kt + \alpha}$ when $\alpha = 1/q_e$, then Blanchard equation simplifies to	[6]
	$q = \frac{q_e^2 kt}{1 + kq_e t}$	
Ho	$q = \frac{q_e^2 kt}{1 + kq_e t}$	[7]

expression was derived assuming chemisorption and monolayer coverage. Recently, Azizian [10] derived the pseudo-second order expression in a more reasonable way supporting the theoretical assumptions of Ho pseudo-second order model. Fig. 1 shows the experimental kinetic data and the predicted kinetics of Ritchie, Sobkowsk and Czerwiński, Blanchard et al. and Ho pseudo-second order model by non-linear method. The obtained kinetic parameters at different initial dye concentrations were shown in Table 2. From Fig. 1, as expected, it was observed that the predicted Ritchie and Sobkowsk and Czerwiński's kinetics exactly overlapped each other with same coefficient of determination values (Table 3). Similarly the Ho pseudo-second order kinetics exactly overlapped the Blanchard et al. kinetics with the same coefficient of determination, r^2 . Table 1 also shows the calculated rate constant k , predicted q_e by Blanchard et al. and Ho pseudo-second order expression were the same. In addition the relatively higher r^2 values (Table 2) of Ho and Blanchard et al. kinetics when compared to that of Ritchie and Sobkowsk and Czerwiński's kinetics confirms Ho and Blanchard et al.

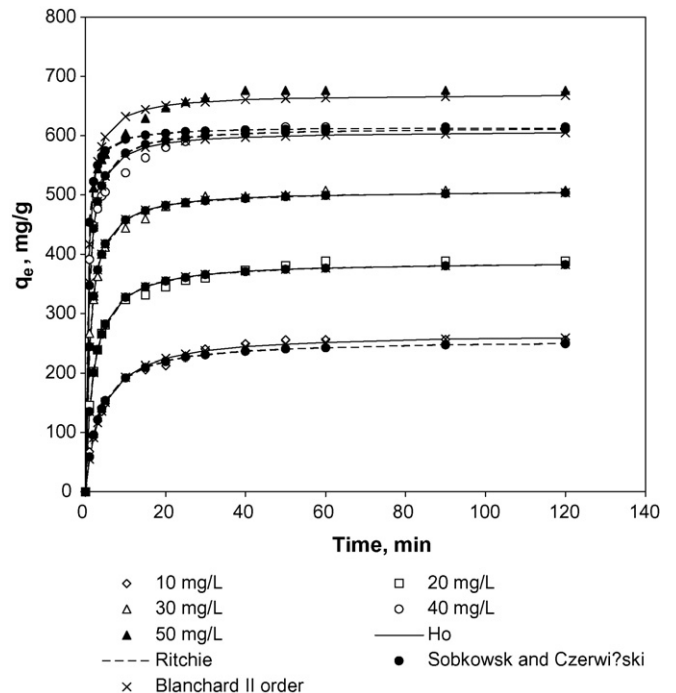


Fig. 1. Sorption kinetics for safranin onto activated carbon by non-linear regression method.

second order expression as the best-fit expression to represent the kinetics of safranin onto activated carbon particles. Though the non-linear method produced similar outcomes for Blanchard et al. and Ho kinetics, the different outcomes obtained by linear regression showed the complexities in using the linear method. In addition from Table 1, the higher r^2 values for Ritchie, Sobkowsk and Czerwiński, Blanchard et al. kinetics by non-linear method when compared to that of r^2 values obtained by linear method suggests that non-linear method as a better option to predict the best-fit kinetics. The difference in r^2 values obtained by linear and non-linear method for the same kinetic expression are due to the error alterations while transforming the data that represents a non-linear kinetics to a linearized form. The linear method assumes that the scatter of points around the trend line follows a Gaussian distribution and the error distribution is the same at every value of X [9]. But this is rarely true or practically impossible with kinetics (as most of the adsorption kinetics are non-linear due to different mechanisms) as the error distribution gets altered after transforming data to a linearized form. Though the error distribution for each experimental data point may be approximately constant over the range of measurement, when linearized to different form the error distribution associated with each data point becomes dependent on its magnitude. This can be observed in the case especially when data are inverted, as in transformations such as in Blanchard et al. expression. This can be visualized from the poor fit and best fit of experimental kinetic data (Table 2) in the linearized expression by Blanchard et al. and Ho. Thus non-linear is better way to obtain the kinetic parameters involved in the Ritchie, Blanchard et al. and Sobkowsk and Czerwiński's second order kinetics. From Table 3, it was observed that both Ritchie and Sobkowsk and Czerwiński kinetics transforms to a linear relation. Similarly the Ho and Blanchard et al. kinetics transforms to a single non-linear form. But from Table 2 it was observed that the calculated k values and the r^2 values for Ritchie and Sobkowsk and Czerwiński kinetics varied. Likewise the k values and the r^2 values obtained from Ho and Blanchard et al. kinetics gets varied. The difference in the calculated k and also the r^2 values are due to the different axial settings, which will alter the error distribution and also on the determined kinetic parameters. However the non-linear method would be avoiding these errors. Thus non-linear is better way to obtain the kinetic parameters involved in the Ritchie, Blanchard et al. and Sobkowsk and Czerwiński's second order kinetics. The best fit of experimental kinetic data in both the linearized and non-linear form of Ho pseudo-second order expression suggests that non-linear and the linearized form proposed by Ho can be used to predict the kinetic parameters involved in the kinetic expression.

More importantly from Table 2, it can be observed that by linear method, the Blanchard et al. expression produced negative

q_e values which is practically impossible. Though the non-linear method proved that both Blanchard et al. and Ho expression were the same, the violation of theory behind the theory of adsorption by Blanchard et al. expression showed that simple linearization process sometimes may seriously affect the kinetic adsorption theory.

In addition while comparing the non-linearized form of Ritchie and Ho expression; it is clear that Ho has different idea on the pseudo-second order kinetics. Recently several arguments have been proposed against the Ho pseudo-second order model by several researchers. A comment has been raised on Ho's expression stating that Ho second order kinetics as a modified expression of Ritchie's expression [11]. In addition, Ho expression was also called as Ritchie's model in some publication [12]. But in the present study, based on the non-linear form for Ritchie and Ho pseudo-second order expression (Table 3) and also based on the obtained kinetics (Table 2), we would like to point out that Ho expression is no where related to Ritchie's kinetic expression. Additionally we would like to point out that the expression relating t/q versus t (Table 1) was proposed by Ho and McKay [7,8] and not by Ritchie [4], Sobkowsk and Czerwiński [5] and Blanchard et al. [6].

4. Conclusions

Linear and non-linear regression analysis showed that Ho pseudo-second order expression as the better expression to predict the kinetics of safranin/activated sorption system. Both linear and non-regression analysis showed that Ritchie and Sobkowsk and Czerwiński have same idea on the second order kinetic expression. Non-linear regression showed that Ho and Blanchard et al. have a similar idea on the pseudo-second order expression but with different assumptions. Present investigation further showed that non-linear method as a better way to predict the optimum sorption kinetics.

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