

Pseudo second order kinetics and pseudo isotherms for malachite green onto activated carbon: Comparison of linear and non-linear regression methods

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Abstract

Pseudo second order kinetic expressions of Ho, Sobkowsk and Czerwinski, Blanchard et al. and Ritchie were fitted to the experimental kinetic data of malachite green onto activated carbon by non-linear and linear 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 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. The amount of dye adsorbed at equilibrium, q_e , was predicted from Ho pseudo second order expression and were fitted to the Langmuir, Freundlich and Redlich Peterson expressions by both linear and non-linear method to obtain the pseudo isotherms. The best fitting pseudo isotherm was found to be the Langmuir and Redlich Peterson isotherm. Redlich Peterson is a special case of Langmuir when the constant g equals unity.

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1. Introduction

Adsorption processes are 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. Search for best-fit kinetic expression is the most common way to predict the optimum sorption kinetic expression. The most commonly used kinetic expressions were the first order [1], second order [1], reversible first order kinetics [2] which are based on the solute concentration. In addition to these kinetic models, several kinetic expressions based on the sorbent concentration such as pseudo first order [3] and pseudo second order [4–7] were also reported. 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 and McKay pseudo second order kinetic model to various sorption systems were made earlier [8]. Further the applicability of the Ho and McKay pseudo second order kinetics for designing multistage sorption systems were also previously reported [9]. A 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 second order [5] and Blanchard et al. second order [6]. The Ritchie model assumes that the rate of adsorption depends solely on the fraction of sites, θ , unoccupied at time t . 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. 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

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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 on solute concentration, Ho and McKay mentioned 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 malachite green onto activated carbon. Malachite green/activated carbon systems were selected as model systems in order to analyze the different pseudo second order models available in literature. A comparison of linear and non-linear method was made to predict the optimum sorption kinetics and also to obtain the kinetic parameters. In addition, the best-fit isotherm was predicted using the pseudo equilibrium data predicted from the best-fit second order kinetic expression.

2. Experimental

The solute used in all the experiments was malachite green, a basic (cationic) dye was obtained from Ranbaxy Chemicals, Mumbai. The adsorbent powdered activated carbon was obtained commercially from E-Merck Ltd, Mumbai. The details of the activated carbon used in the present study was discussed elsewhere [10].

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 at 2500 rpm for 10 min and the concentration in the supernatant solution was analyzed using UV spectrophotometer at maximum absorbance wavelength of 620 nm.

3. Results and discussions

In the present study the best fit of a kinetic expression or equilibrium expression to the experimental data were tested using the value of coefficient of determination, r^2 , which is defined as:

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

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 form and the non-linear form of the different pseudo second order kinetic expressions are 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 model were obtained from the plot between $q_e/(q_e - q)$ versus time t , $\theta/(1 - \theta)$ versus time 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 much 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 malachite green 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 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, r^2 , 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

Table 1
Linearized forms of second order models

Author	Year	Non-linear form	Linear form	Plot	Reference
Sobkowsk and Czerwiński	1974	$q = \frac{q_e kt}{kt + 1}$	$\frac{\theta}{1 - \theta} = k_2 t$	$\frac{\theta}{1 - \theta}$ vs. t	[5]
Ritchie	1977	$q = \frac{q_e kt}{kt + 1}$	$\frac{q_e}{q_e - q} = kt + 1$	$\frac{q_e}{q_e - q}$ vs. t	[4]
Blanchard et al.	1984	$q = \frac{ktq_e + \alpha q_e - 1}{kt + \alpha}$ when $\alpha = 1/q_e$, then Blanchard eqn simplifies to: $q = \frac{q_e^2 kt}{1 + kq_e t}$	$\frac{1}{q_e - q} - \alpha = kt$	$\frac{1}{q_e - q}$ vs. t	[6]
Ho	1995	$q = \frac{q_e^2 kt}{1 + kq_e t}$	$\frac{t}{q} = \frac{1}{kq_e^2} + \frac{1}{q} t$	$\frac{t}{q}$ vs. t	[7]

Table 3
Isotherms and their linear forms (q_m : mg/g; K_a : L/mg; K_F : (mg/g)(L/g)ⁿ; A : L/g; B : L/mg^{1-1/A})

Isotherm	Linear form	Plot	Reference
Freundlich	$q_e = K_F C_e^{1/n}$	$\log(q_e) = \log(K_F) + 1/n \log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$ [14]
Type 1 Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{q_e}$ vs. C_e	[15]
Type 2 Langmuir	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	$\frac{1}{q_e} = \left(\frac{1}{K_a q_m} \right) \frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$
Type 3 Langmuir	$q_e = q_m - \left(\frac{1}{K_a} \right) \frac{q_e}{C_e}$	q_e vs. $\frac{q_e}{C_e}$	
Type 4 Langmuir	$\frac{q_e}{C_e} = K_a q_m - K_a q_e$	$\frac{q_e}{C_e}$ vs. q_e	
Redlich Peterson	$q_e = \frac{A C_e}{1 + B C_e^g}$	$\ln \left(A \frac{C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(B)$	$\ln \left(A \frac{C_e}{q_e} - 1 \right)$ vs. $\ln(C_e)$ [16]

cles. Though the non-linear method produced similar outcomes for Blanachard et al. and Ho kinetics, the different outcomes obtained by linear regression showed the complexities in using the linear method. In addition from Table 2, the higher r^2 values for Ritchie, Sobkowsk and Czerwiński, Blanachard 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 . 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. From Table 1, it was observed that both Ritchie and Sobkowsk and Czerwiński kinetics transforms to a linear relation. Similarly the Ho and Blanachard 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 Blanachard 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, Blanachard 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.

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 [12]. In addition, Ho expression was also called as Ritchie's model in some publication [13]. But in the present study, based on the non-linear form for Ritchie and Ho pseudo second order expression (Table 1) 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 linearized form of pseudo second order expression as shown in Table 1 was proposed by Ho and not by Ritchie [4], Sobkowsk and Czerwiński [5] and Blanachard et al. [6].

The present study showed that the Ho pseudo second order can be used to predict the amount of dye adsorbed at equilibrium, q_e . From the q_e values obtained using the Ho's pseudo second order model, the equilibrium solute phase concentration in liquid can be obtained from the mass balance equation as follows:

$$C_e = C_0 - \frac{q_e M}{V} \quad (2)$$

where C_0 is the initial solute concentration, mg/L; C_e the equilibrium solute concentration in liquid phase, mg/L, M the mass of the adsorbent, g; and V is the volume of the solution, L.

The predicted equilibrium data from pseudo second order kinetics were fitted to the three widely used isotherms, Freundlich [14], Langmuir [15] and Redlich and Peterson [16] isotherms. A similar attempt of developing the pseudo isotherms was previously reported by Ho and Wang [17] for sorption of cadmium ions onto tree fern and also by Ho [18] for four different sorbate systems such as Cu/tree fern, Pb/tree fern, AB9/activated clay and BR18/activated clay systems. Table 3 shows the different linearized forms and the non-linear form of Freundlich, Langmuir and Redlich Peterson isotherms. From Table 3 it was observed that Langmuir isotherm can be linearized to at least to four types. Table 4 show the predicted the isotherm constants and the corresponding r^2 values. From the Table 4, it was observed that the isotherm parameters obtained from the four linearized Langmuir isotherm were different. Type 1 and Type 2 Langmuir isotherm was found to be the best fitting linearized Langmuir expression. Type 3 and Type 4 poorly represents the pseudo equilibrium experimental data of malachite green onto activated

Table 4
Calculated pseudo isotherm parameters by linear and non-linear method

Linear method			Non-linear method
Freundlich		$K_F, (\text{mg/g})(\text{L/g})^n$	56.89288
		$1/n$	0.39957
		r^2	0.946339
Langmuir	Type 1	$q_m, \text{mg/g}$	469.8278
		$K_L, \text{L/g}$	0.031013
		r^2	0.99498
	Type 2	$q_m, \text{mg/g}$	490.7659
		$K_L, \text{L/g}$	0.027571
		r^2	0.991222
	Type 3	$q_m, \text{mg/g}$	480.1297
		$K_L, \text{L/g}$	0.029173
		r^2	0.959769
	Type 4	$q_m, \text{mg/g}$	487.8128
		$K_L, \text{L/g}$	0.028
		r^2	0.959769
Redlich Peterson	A	13.7295	14.08012
	B	0.028254	0.029351
	g	1	1
	r^2	0.994262	0.983983

carbon with same coefficient of determination of 0.9597. When comparing the r^2 value of Freundlich, Langmuir and Redlich Peterson isotherm Type 1, Type 2 Langmuir and Redlich Peterson isotherms were found to be the best-fitting isotherm for the pseudo equilibrium data of malachite green onto activated carbon. The relatively lower values of Freundlich isotherm showed that it is inappropriate to use this expression to represent the malachite green by activated carbon at equilibrium conditions. In addition, the value of $g=1$ indicates that isotherm is approaching Langmuir instead of Freundlich isotherm. Though the present investigation showed that linear method as a reasonable approach to predict the optimum pseudo sorption isotherm, the different outcomes by the four type of Langmuir isotherm for the same experimental equilibrium data shows the complexities in selecting the optimum sorption isotherm. This is because the linear method doesn't take advantage to minimize the error distribution if the experimental error appears in both X and Y direction and just reports the Y data with respect to the X based on the linearized form we use. Since there is a different axial settings (both X and Y) in the four linearized types of Langmuir isotherms which may lead to different expression that relate the Y with X . In order to avoid such errors due to linearization, pseudo equilibrium data were further fitted to the Langmuir, Freundlich and Redlich Peterson isotherms by non-linear method.

For non-linear method, a trial and error procedure, which is applicable to computer operation, was used to determine the equilibrium parameters by maximizing the respective the coefficient of determination between experimental data and pseudo equilibrium using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel. Fig. 2 shows the experimental data and the fitted pseudo isotherms for the sorption of malachite green onto activated carbon particles. The calculated isotherm parameters by non-linear method were shown in Table 4. From Table 4, it was observed that the calculated isotherm parameters for the

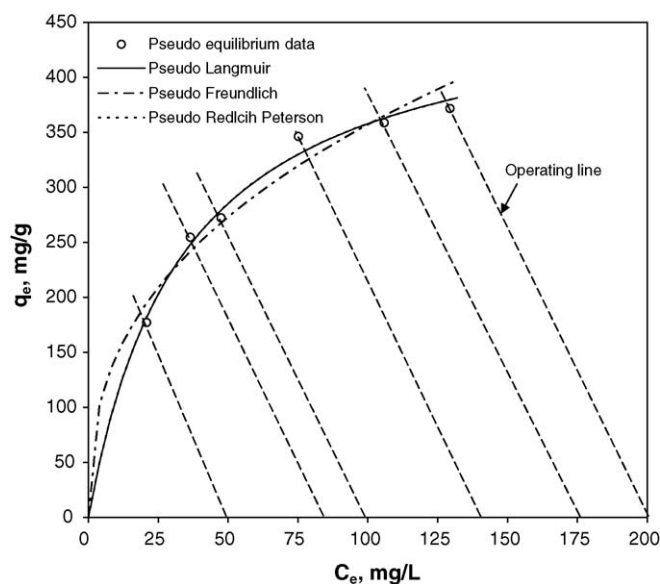


Fig. 2. Pseudo isotherms for malachite green onto activated carbon at 305 K.

four linearized form of Langmuir isotherms were the same by non-linear method. The higher r^2 value of 0.9839 for both Langmuir and Redlich Peterson isotherm shows the applicability of these models. Further from Fig. 2, it was observed that pseudo Langmuir exactly overlapped the pseudo Redlich Peterson with the same coefficient of determination r^2 . Thus, Langmuir is a special case of Redlich Peterson isotherm when the constant g equals unity.

4. Conclusions

Linear and non-linear regression analysis showed that Ho pseudo second order expression as the better expression to

predict the kinetics of malachite green/activated sorption system. Both linear and non-linear 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. Pseudo Freundlich, pseudo Langmuir and pseudo Redlich Peterson isotherms have been derived and reported using the q_e values obtained from Ho pseudo second order kinetics. Present investigation further showed that non-linear method as a better way to predict the optimum sorption kinetics and also the optimum pseudo isotherm. Redlich Peterson is a special case of Langmuir when the constant g equals unity.

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