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PSEUDO-SECOND-ORDER KINETIC MODEL FOR SORPTION OF MALACHITE GREEN ONTO SEA SHELL: COMPARISON OF LINEAR AND NON-LINEAR METHODS

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ABSTRACT

In this study, the sorption of malachite green, a basic dye onto sea shell was studied by performing batch kinetic sorption experiments. The equilibrium kinetic data were analyzed using the pseudo-second-order kinetic model. A comparison between linear least-squares method and non-linear regression method of estimating the kinetic parameters was examined. Four pseudo-second-order kinetic linear equations were discussed. Kinetic parameters obtained from four kinetic linear equations using the linear method differed. Type 1 pseudo-second-order kinetic model very well represented the kinetic uptake of malachite green by sea shell while Type 4 exhibited the worst fit. Present investigation showed that the non-linear method may be a better way to determine the kinetic parameters.

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Keywords: *malachite green; sea shell; pseudo-second-order, linear method; non-linear method*

[I] INTRODUCTION

Adsorption often referred to as passive uptake and physico-chemical binding of chemical species or ions to a solid surface, is now widely accepted as an efficient and economically feasible process for the removal of synthetic dyes from industrial effluents. The next real challenge in the adsorption field is to identify the adsorption mechanism. Therefore an extensive study of the adsorption kinetics is important since the kinetics describe the uptake rate of adsorbate which in turn helps to predict the adsorption mechanism. Several researchers have used different kinetic models to predict the mechanism involved in the sorption process. These include pseudo-first-order model, pseudo-second-order model, Weber and Morris sorption kinetic model, first-order reversible reaction model, external mass transfer model, first-order equation of Bhattacharya and Venkobachar, Elovich's model and Ritchies's equation [1]. Literature analysis shows that though several kinetic models are available, except the pseudo-second-order model, no other model represents well the experimental kinetic data for the entire sorption period for most of the systems. In recent years, linear regression is frequently used to determine the best-fitting kinetic equation.

An accuracy of a kinetic model is generally a function of the number of independent parameters, while its popularity in relation to the process application is an indicative of its mathematical simplicity. Likewise, linear regression is frequently used to determine the best-fitting kinetic equation primarily owing to its wide usefulness in a variety of adsorption data and partly reflecting the appealing simplicity of its equations. The linear least-squares method with linearly transformed kinetic rate equation has also been widely applied for confirming the experimental data using coefficients of determination. The kinetic equation giving a coefficient of determination closest to unity is considered to be the best fitting. However, during the last few years, a development interest in the utilization of nonlinear optimization modeling has been noted. This is mainly because such transformation of non-linear equations to linear forms implicitly alters their error structure and may also violate the error variance and normality assumptions of standard least squares [2]. As a result, one may obtain different kinetic parameters when using different forms of a kinetic model for a given sorption process. On the contrary, the non-linear method for analyzing the experimental data provides a more complex mathematical method for determining kinetic parameters and is conducted on the same abscissa and ordinate, thus avoiding the drawbacks of linearization.

With the aforementioned, the present study attempts a comparative analysis between the linear least-square and non-linear regression method of the widely used pseudo-second-order to predict the best sorption kinetics and also to obtain the kinetic parameters using the experimental data of malachite green onto sea shell. The present work is aimed at evaluating the accuracy and consistency in parameter prediction by the linear and non-linear method, and to familiarize the knowledge deficiencies regarding non-linearized adsorption kinetics.

[II] MATERIALS AND METHODS

2.1. Adsorbent

Bivalve type sea shells that most commonly wash up on large sandy beaches were used in this study. The sea shells were collected from the sea beaches of Puri, Orissa, India. It was pretreated before use by washing thoroughly with double distilled water and dried at 110 ± 1 ^{0}C for 24 h in an oven drier. The raw biosorbent was crushed and ground using ball mill and sieved to give a fraction of 80 mesh. The biosorbent was again washed thoroughly with distilled water and dried naturally. The resulted shell particles were stored in sterile, sealed glass containers and used in all the adsorption experiments.

2.2. Adsorbate

Malachite Green used in this study was of commercial quality (CI 42000, FW: 365, MF: $C_{23}H_{25}N_2Cl$) and was used without further purification. Stock solution (500 mg L^{-1}) was prepared by dissolving accurately weighed quantity of the dye in double-distilled water. All working solutions were prepared by diluting the stock solution with suitable volume of double-distilled water.

2.3. Adsorption experiments

Adsorption kinetics experiments were carried out using the batch method for different initial dye concentrations. The experiments were carried out in 250 mL Erlenmeyer flasks containing a fixed amount of adsorbent with 100 mL dye solution. Adsorption kinetics was conducted using the batch method. The initial pH of the solution was adjusted with 0.1 N HCl or NaOH solutions by using a pH meter. The flasks were agitated and incubated in an incubator shaker (Model Innova 42, New Brunswick Scientific, Canada) at 30 ± 1 ^{0}C until reaching equilibrium. Samples were taken from the flasks at regular time intervals for analyzing the concentration of malachite green in the solution. The residual amount of malachite green in each flask was investigated using UV/VIS spectrophotometer (Model Hitachi – 2800) at λ_{max} of 663 nm.

2.3. Pseudo-second-order kinetic model

The pseudo-second order kinetic equation was proposed by Blanchard et al. [3] and is expressed as:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad \text{-------------------------- (1)}$$

where q_t and q_e are the amount of dye adsorbed at time t and at equilibrium (mg.g^{-1}) and k_2 (g. mg^{-1} min^{-1}) is the pseudo-second-order rate constant for the adsorption process. Eq. (1) can be linearized to at least four different forms [4]. The different linearized forms of the pseudo-second-order equation are given in **Table-1**. The most popular form used is Type 1 [1].

Table 1: Different linearized forms of the pseudo-second-order equation

Linear Regression	Expression	Plot
Type 1	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	t / q_t vs. t
Type 2	$\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2} \frac{1}{t}$	$1/ q_t$ vs. $1/$
Type 3	$q_t = q_e - \frac{1}{k_2 q_e} \frac{q_t}{t}$	q_t vs. q_t / t
Type 4	$\frac{q_t}{t} = k_2 q_e^2 - k_2 q_e q_t$	q_t / t vs. q_t

[III] RESULTS

In the present study, the coefficient of determination (r^2) was used to determine the best fit equation:

$$r^2 = \frac{(q_{e,meas} - \overline{q_{e,cal}})^2}{\sum (q_{e,meas} - \overline{q_{e,cal}})^2 + (q_{e,meas} - q_{e,cal})^2} \qquad \text{---- (2)}$$

where $q_{e,meas}$ and $q_{e,cal}$ (mg.g^{-1}) are the measured and calculated adsorbate concentration at equilibrium, and $\overline{q_{e,cal}}$ (mg.g^{-1}) is the average of $q_{e,cal}$ (mg.g^{-1})

Linear regression is frequently used to determine the best fitting kinetic model, and the method of least squares is used for finding the parameters of the kinetic models. The pseudo second-order kinetic constant, q_e and k_2 by a Type 1 pseudo second-order expression were calculated from the plot of t/q_t versus *t* as shown in **Figure-1**. Similarly the pseudo-second-order kinetic constant, q_e and k_2 were obtained from the plot of 1/ $q_{,t}$ and 1/t, q_t and q_t/t, q_t/t and q_t for a Type 2, Type 3, and Type 4 pseudo second-order expressions respectively. The calculated kinetic constants and their corresponding coefficient of determination (r^2) are given in **Table-2.** The experimental q_e value is also shown in **Table-2**. **Table-2** shows that q_e and k_2 values obtained from the four linear forms of pseudo-second-order expressions were different at all initial dye concentration studied. From **Table-2**, it was observed that except Type 1 pseudo-second-order expression, no other model provided a better fit to the experimental kinetic data. The very low r^2 values for Type 2-4 pseudo-

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second-order expressions suggest that it was not appropriate to use these models to represent the experimental data of malachite green onto sea shell. Therefore, by linear method, a theoretical pseudo-second-order model was found to aptly represent the experimental data based on Type 1 pseudo-second-order kinetic expression. In addition, the Type 1 pseudo second order expression predicts reasonably the *q*e values theoretically for all the range of initial dye concentrations studied **Table-1**.

In the case of the non-linear method, the software Origin version 9.0 was used for determining the pseudo-second-order kinetic parameters. Pseudo-second-order kinetic parameters obtained by non-linear method are enlisted in **Table-2**. **Figure-2** shows experimental data and the predicted pseudo-second-order kinetics using the non-linear method. Very high r^2 value suggests that the non-linear pseudo-second-order kinetic model could be used to represent the kinetic uptake of malachite green onto sea shell at all initial dye concentrations studied. By using non-linear method there were no problems with transformation of non-linear pseudo-second-order equation to linear form, and also they were in the same error structures. It is thus logical to use the non-linear method to represent a kinetic model efficiently and effectively.

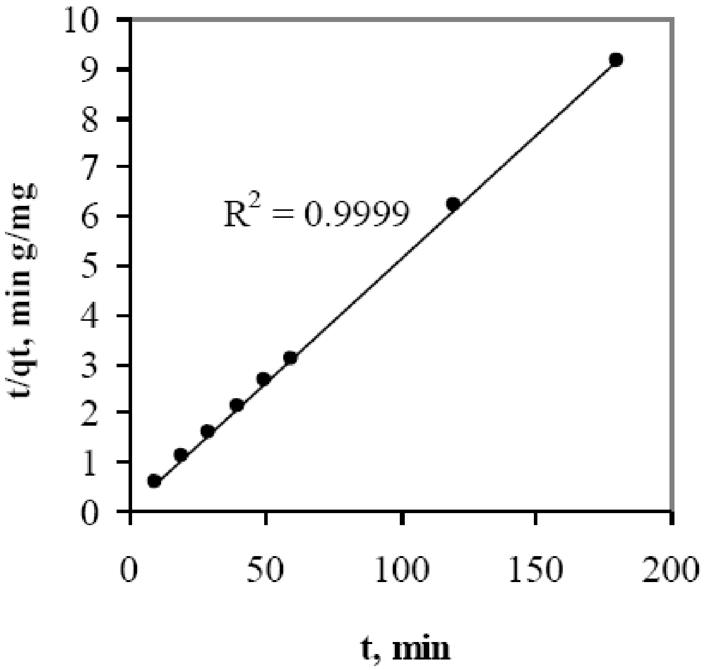

Fig: 1. Type 1 pseudo-second-order kinetics obtained by using the linear method for the sorption of methylene blue onto sea shell (C_0=50 mg L^{-1})

[IV] DISCUSSION

In most adsorption studies, the linear method has been widely used in assaying the quality of fit of a kinetic model to an experimental data primarily due to its simplicity and usefulness. However, the different outcomes obtained by linear regression for the same kinetic model show the real complexities and problems in estimating the kinetic parameters by linearization technique.

The different outcomes for different linearized form of pseudo-second-order models are due to the error alterations while transforming the data that represents a non-linear kinetics to a linearized form. The transformation of a non-linear model to a linear one primarily distorts the normality assumptions of the linear least square method. In addition, a different axis setting alters the regression results, thereby influencing the accuracy as well as consistency, leading to the violation of theories behind the kinetic models. Moreover, the linear method does not test the linearity of the data set. Instead, it assumes that the given data set were linear and gives a straight line that predicts the goodness of fit of the equilibrium experimental data. Furthermore, the linear method is based on the assumption that the scatter vertical points around the line follows a Gaussian distribution, and the error distribution is uniform at every value of X-axis. This is rarely true or practically impossible with kinetics as most of the adsorption kinetic models are non-linear due to different mechanisms.

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Table 2: Pseudo-second-order kinetic parameters obtained by using the linear and non-linear methods

Kinetic Model	Parameters	C_0 (mg L^{-1})			
		50	**100**	**150**	**200**
	$q_{e,exp}$ (mg g^{-1})	46.27	82.55	135.89	152.56
Linear-Type 1	q_e (mg g^{-1})	45.67	83.78	137.32	150.98
	k_2(g $mg^{-1}min^{-1}$)	0.0448	0.0540	0.0610	0.0689
	r^2	0.998	0.999	0.990	0.991
Linear- Type 2	q_e (mg g^{-1})	45.14	85.13	132.52	154.39
	k_2(g $mg^{-1}min^{-1}$)	0.0384	0.0516	0.0602	0.0632
	r^2	0.975	0.972	0.969	0.981
Linear-Type 3	q_e (mg g^{-1})	45.02	79.20	130.21	150.47
	k_2(g $mg^{-1}min^{-1}$)	0.0324	0.0578	0.0592	0.0667
	r^2	0.954	0.963	0.923	0.956
Linear-Type 4	q_e (mg g^{-1})	45.36	87.53	129.38	156.62
	k_2(g $mg^{-1}min^{-1}$)	0.0352	0.0521	0.0621	0.0732
	r^2	0.863	0.838	0.762	0.803
Non-linear	q_e (mg g^{-1})	46.17	82.91	135.42	152.87
	k_2(g $mg^{-1}min^{-1}$)	0.0578	0.0621	0.0732	0.0771
	r^2	1.000	0.999	1.000	1.000

The linear method considers error distribution only along the Y-axis irrespective of the corresponding X-axis resulting in the different determined parameters for the four different types of linearized pseudo-second-order kinetic model for the same experimental data. Therefore the linear method is inappropriate in predicting the best-fit kinetics for a particular experimental data set and unable for providing a fundamental understanding of the kinetics of the adsorption systems, resulting in an improper conclusion. On the contrary, the drawbacks of linear method can be avoided by adopting the non-linear method for analyzing the experimental data. This is because in the non-linear method, the experimental equilibrium data and the isotherms are in a fixed x and y axis i.e, the non-linear analysis is conducted on the same abscissa and ordinate resulting in the same error distribution and structure.

The present investigation confirms the non-linear method as an appropriate technique to predict the optimum sorption kinetics. Ho (2006) conducted a similar evaluation using linear and non-linear methods to determine the pseudo-second-order kinetic parameters [5]. He chose cadmium as the adsorbate and tree fern as the adsorbent. The kinetic parameters acquired from the four kinetic linear equations using linear method had discrepancies among themselves. Further, for linear method, the best fit was obtained by using the Type 1 expression because the highest coefficient of determination was calculated from the fitted equation. In contrast to the linear method, kinetic parameters obtained from the four kinetic linear equations were the same when using the non-linear method. Under such conditions, it would be more rational and reliable to interpret adsorption data through a process of nonlinear regression.

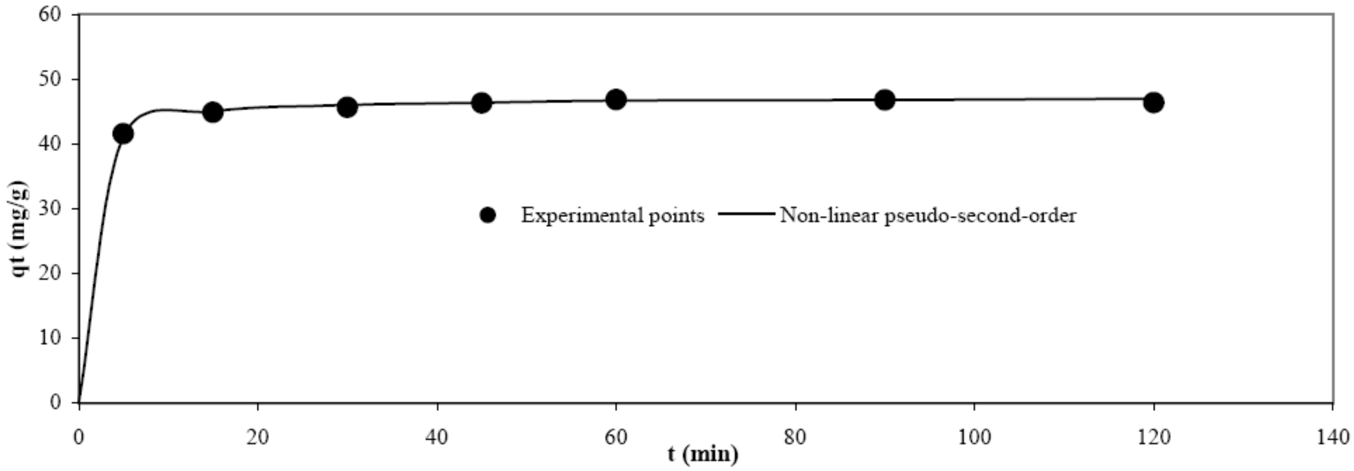

Fig: 2. Pseudo-second-order kinetics obtained by using the non-linear method for the sorption of methylene blue onto shell (C_0=50 mg L^{-1})

[V] CONCLUSION

A comparative analysis between the linear and non-linear method in determining the pseudo-second-order kinetic parameters for sorption of methylene blue onto sea shell was conducted. Present study corroborated that it is not appropriate to use the linear method in determining kinetic parameters of a particular kinetic model. This is mainly because transforming a non-linear kinetic model to a linearized form tends to alter the error distribution, and thus distort the parameters. Non-linear analysis conducted on the same abscissa and ordinate results in the same error distribution and is therefore a better way to obtain the kinetic parameters than linear method.

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