Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon

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Abstract

Batch kinetic experiments were carried out for the sorption of methylene blue onto activated carbon. The experimental kinetics were fitted to the pseudo first-order and pseudo second-order kinetics by linear and a non-linear method. The five different types of Ho pseudo second-order expression have been discussed. A comparison of linear least-squares method and a trial and error non-linear method of estimating the pseudo second-order rate kinetic parameters were examined. The sorption process was found to follow a both pseudo first-order kinetic and pseudo second-order kinetic model. Present investigation showed that it is inappropriate to use a type 1 and type pseudo second-order expressions as proposed by Ho and Blanachard et al. respectively for predicting the kinetic rate constants and the initial sorption rate for the studied system. Three correct possible alternate linear expressions (type 2 to type 4) to better predict the initial sorption rate and kinetic rate constants for the studied system (methylene blue/activated carbon) was proposed. Linear method was found to check only the hypothesis instead of verifying the kinetic model. Non-linear regression method was found to be the more appropriate method to determine the rate kinetic parameters.

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Keywords: Adsorption; Methylene blue; Activated carbon; Adsorption kinetics; Pseudo second-order; Linear method; Non-linear method

1. Introduction

Sorption processes are proved to be an effective method for the treatment of dye wastewaters [1,2]. Activated carbon is the most commonly used adsorbent for the removal of dye ions from its aqueous solution [3]. The prediction of batch sorption kinetics is necessary for design of industrial adsorption column [1]. 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 systems and also on the system conditions. The most commonly used kinetic expressions to explain the solid/liquid adsorption processes are the pseudo first-order kinetics and pseudo second-order kinetic model [1,2,4]. External mass transfer and intraparticle diffusion model were also used to predict the sorption kinetics [2,5,6]. Multiple first-order kinetics have been reported for protein/silica system [7]. Previously researchers [1,2] found that the Lagergren pseudo first-order kinetics was found to well represent the experimental kinetic data where the probable sorbate interactions were expected to be negligible. Lagergren pseudo first-order kinetics are not proved to be effective in representing the experimental kinetic data for the entire sorption period [1,2]. In some cases though the Lagergren pseudo first-order kinetics provide excellent fit with the experimental kinetic data, it failed to predict the $q_e$ theoretically thereby deviating from the theory [8]. External mass transfer and intraparticle diffusion will represent the experimental kinetics where the effect of pore diffusion and film diffusion are expected to negligible respectively. Recently the pseudo second-order expression as proposed by Ho [9] was found to well explain the kinetics of the most of sorption systems very well for the entire range of sorption period. The Ho pseudo second-order expression was found to show a better fit towards the sorption of heavy metals [10], dyes onto adsorbent materials of organic nature [11–13] and inorganic nature [14] nature. However a linear pseudo second-order expression proposed by Blanchard et al. [15] with ideas similar to Ho expression was found to poorly represent the sorption system of safralin onto rice husk particles [16]. In the present study an extensive analysis of pseudo second-order expression and pseudo first-order expression was made using the experimen-
tial kinetic data of methylene blue onto activated carbon. Also a comparison of linear and non-linear regression method of estimating the kinetic parameters and optimum kinetics were also discussed.

2. Materials and methods

The dye used in all the experiments was methylene blue, a basic (cationic) dye. The structure of methylene blue (C.I: Basic Blue 9) is given by:

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: ≤ 1%; substances soluble in HCl: ≤ 3%; Cl: ≤ 0.2%; SO4: ≤ 0.2%; heavy metals as Pb: ≤ 0.005%; iron (Fe): ≤ 0.1%; incomplete carbonization: passes test; methylene blue adsorption: ≤ 180 mg/g; loss on drying: ≤ 10%; residue on ignition: ≤ 5%.

So, absorption kinetics experiments were carried out using baffled agitators of 2 L capacity for different initial dye concentrations. 1.5 L of dye solution of known initial dye concentration was agitated with 0.66 g of activated carbon at room temperature (32 °C) at a pH of 8 and at a constant agitation speed of 800 rpm. A 2.5 mL of samples were pipetted out using 10 mL syringe agitators of 2 L capacity for different initial dye concentrations.

180 mg/g; loss on drying: ≤ 10%; residue on ignition: ≤ 5%.

Some of the specifications of the activated carbon used in the present study were discussed.

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\[
\text{H}_3\text{C} - \text{N} - \text{CH}_3 \quad \text{(CT)} \quad \text{N} - \text{CH}_3
\]

The stock solution of methylene blue was prepared by dissolving 1 g of methylene blue in one liter of distilled water. All working solutions of desired concentrations were prepared by diluting the stock solution with distilled water.

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The kinetic rate equations can thus be rewritten as follows:

\[
\frac{dq}{dt} = K_2 (q_e - q)^2
\]

where \( K_2 \) is the rate of sorption (g/mg min), \( q_e \) the amount of dye adsorbed onto activated carbon at equilibrium (mg/g) and \( q \) the amount of dye adsorbed at any time (mg/g). Separating Eq. (2), gives:

\[
\frac{dq}{(q_e - q)^2} = K_2 dt
\]

Integrating Eq. (3) for boundary conditions \( t=0 \) and \( t=t \) and \( q = 0 \) and \( q = q_e \), gives [15]:

\[
\frac{1}{q_e - q} = \frac{1}{q_e} + K_2 t
\]

which is the integrated rate law for pseudo-second reaction.

\[
\text{Type 2 pseudo-second-order}
\]

\[
q = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}
\]

\[
\frac{1}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}
\]

\[
1/t = \frac{1}{q_e} + \frac{1}{q_e}
\]

\[
1/t vs. 1/q \quad q_e = \text{slope}^2/\text{intercept}
\]

\[
\text{Type 3 pseudo-second-order}
\]

\[
q = \frac{K_2 q_e^2}{q}
\]

\[
\frac{1}{q} = K_2 q_e^2 - q_e
\]

\[
1/t vs. 1/q \quad q_e = -1/\text{slope}^2/\text{intercept}, \quad K_2 = \text{intercept}^2/\text{slope}
\]

\[
\text{Type 4 pseudo-second-order}
\]

\[
q = \frac{K_2 q_e^2 q}{q_e}
\]

\[
\frac{1}{q} = q_e^2 - q_e
\]

\[
q/t vs. q \quad q_e = -1/\text{intercept}/\text{slope}, \quad K_2 = \text{slope}^2/\text{intercept}
\]

\[
\text{Type 5 pseudo-second-order}
\]

\[
q = \frac{K_2 q_e^2}{q_e}
\]

\[
\frac{1}{q} = K_2
\]

\[
1/(q_e - q) vs. t \quad q_e = 1/\text{intercept}, \quad K_2 = \text{slope}
\]

3. Results and discussions

For adsorption system following the pseudo second kinetics, the adsorbate was assumed to get adsorbed onto two surface sites. Thus the sorption kinetics following pseudo second-order kinetics can be represented as

\[
\frac{d(AC)_t}{dt} = K[(AC)_0 - (AC)_t]^2
\]

where 

\[
(AC)_t \quad \text{and} \quad (AC)_0 \quad \text{number of active sites}
\]

occupied on the activated carbon at any time and \( (AC)_0 \) is the number of active sites available on the adsorbent surface.

The kinetic rate equations can thus be rewritten as follows:

\[
\frac{dq}{dt} = K_2 (q_e - q)^2
\]

where \( K_2 \) is the rate of sorption (g/mg min), \( q_e \) the amount of dye adsorbed onto activated carbon at equilibrium (mg/g) and \( q \) the amount of dye adsorbed at any time (mg/g). Separating Eq. (2), gives:

\[
\frac{dq}{(q_e - q)^2} = K_2 dt
\]

Integrating Eq. (3) for boundary conditions \( t=0 \) and \( t=t \) and \( q = 0 \) and \( q = q_e \), gives [15]:

\[
\frac{1}{q_e - q} = \frac{1}{q_e} + K_2 t
\]

which is the integrated rate law for pseudo-second reaction.

\[
\text{Eq. (4) can be linearized to at least four more different linear forms as shown in Table 1. Table 1 also shows the non-linear form of Eq. (4). A type 1 expression as shown in Table 1 was previously reported by Ho [9] for the sorption of divalent metal ions onto zeolite particles. A type 5 expression as in Table 1 was previously reported by Blanchard et al. [15] for the exchange reaction of divalent metallic ions onto NH4+ ions fixed onto zeolite particles.}

Table 1

<table>
<thead>
<tr>
<th>Type</th>
<th>Non-linear form</th>
<th>Linear form</th>
<th>Plot</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>( q = q_e(1 - e^{-Kt}) )</td>
<td>( \log(q_e - q) = \log(q_e) - \frac{K_1 t}{2.303} )</td>
<td>( \log(q_e - q) vs. t )</td>
<td>( K_1 = -2.303 \times \text{slope} )</td>
</tr>
<tr>
<td>Type 1 pseudo-second-order</td>
<td>( t = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} )</td>
<td>( t/q ) vs. ( t )</td>
<td>( q_e = 1/\text{slope}, K_2 = \text{slope}^2/\text{intercept} )</td>
<td></td>
</tr>
<tr>
<td>Type 2 pseudo-second-order</td>
<td>( \frac{1}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} )</td>
<td>( 1/t vs. 1/q )</td>
<td>( q_e = 1/\text{intercept}, K_2 = \text{intercept}^2/\text{slope} )</td>
<td></td>
</tr>
<tr>
<td>Type 3 pseudo-second-order</td>
<td>( \frac{1}{q} = K_2 q_e^2 - q_e )</td>
<td>( 1/t vs. 1/q )</td>
<td>( q_e = -1/\text{slope}/\text{intercept}, K_2 = \text{slope}^2/\text{intercept} )</td>
<td></td>
</tr>
<tr>
<td>Type 4 pseudo-second-order</td>
<td>( \frac{1}{q} = K_2 q_e^2 q / q_e )</td>
<td>( q/t vs. q )</td>
<td>( q_e = -1/\text{intercept}/\text{slope}, K_2 = \text{slope}^2/\text{intercept} )</td>
<td></td>
</tr>
<tr>
<td>Type 5 pseudo-second-order</td>
<td>( \frac{1}{q} = \frac{K_2 q_e^2}{q_e} )</td>
<td>( 1/(q_e - q) vs. t )</td>
<td>( q_e = 1/\text{intercept}, K_2 = \text{slope} )</td>
<td></td>
</tr>
</tbody>
</table>
Likewise the sorption of methylene blue following the first-order kinetics can be represented as

\[ \frac{dq}{dt} = K_1(q_e - q) \]  

Integrating Eq. (5) for boundary conditions \( t = 0 \) and \( t = t \) and \( q = 0 \) and \( q = q_e \), gives [17]:

\[ \log(q_e - q) = \log(q_e) - \frac{K_1 t}{2.303} \]  

For the present study, the experimental kinetic data for methylene blue onto activated carbon were fitted to the five different linearized forms of pseudo second-order model and the linearized pseudo first-order kinetic expression. The non-linear pseudo second-order model and pseudo first-order kinetic model and its linearized expressions were given in Table 1. The pseudo second-order kinetic constant and the theoretical \( q_e \) by a type 1 pseudo second-order expression can be calculated from the plots of \( t/q \) versus \( t \) as shown in Fig. 1. Similarly the pseudo second-order kinetic constant \( K_2 \) and the theoretical \( q_e \) can be obtained from the plot of \( 1/q \) versus \( 1/t \), \( 1/t \) versus \( 1/q \), \( q/t \) versus \( 1/q_e - q \) versus \( t \) for a type 2, type 3, type 4 and type 5 pseudo second-order expressions respectively. The way to obtain the kinetic rate constant \( K_2 \) (mg/mg min), initial sorption rate \( h \) (mg/g min) and the amount of dye adsorbed at equilibrium \( q_e \) (mg/g) are explained in Table 1. The pseudo first-order kinetic constant and the theoretical \( q_e \) based on pseudo first-order kinetics can be obtained from the plot of \( \log(q_e - q) \) versus \( t \). The predicted kinetics from the linear pseudo first-order kinetic expression was shown in Fig. 2. The calculated kinetic constants at different methylene blue concentration were shown in Table 2. From Table 2, it was observed that the \( K_2 \), initial sorption rate, \( q_e \) values obtained from the five linear forms of pseudo second-order expressions were different. The very lower \( r^2 \) values for type 5 pseudo second-order expression suggests that it is not appropriate to use pseudo second model. However the very higher \( r^2 \) values (>0.99 in most of the cases) for type 1 expression at all initial dye concentration studied suggests pseudo second-order kinetic expression was the optimum kinetic expression to represent the methylene blue uptake by activated carbon. By linear method, a theoretical pseudo second-order model was found to well represent the experimental kinetic data of methylene blue onto activated carbon based on a type 1 pseudo second-order kinetic expression. However a type 5 pseudo second-order expression very poorly represents the kinetic data of methylene blue onto activated carbon. In addition a type 1 pseudo second-order expression predicts reasonably the methylene blue uptake by activated carbon. By linear method, a theoretical pseudo second-order model was found to well represent the experimental kinetic data of methylene blue onto activated carbon based on a type 1 pseudo second-order kinetic expression. However the theoretically predicted \( q_e \) values practically for all the range of initial dye concentrations studied (Table 2). However from Table 2, it can be noticed that a type 5 pseudo second-order expression failed to predict the \( q_e \) values theoretically. Thus the theory behind the pseudo second-order kinetics was getting valid for methylene blue/activated carbon system based on a type 1 expression and the theory behind the pseudo second-order kinetics was violated by a type 5 expression. Further for an initial dye concentration of 100 mg/L, a type 5 pseudo second-order expression produced negative \( q_e \) values from the pseudo second-order kinetic theory which is experimentally and practically impossible. In addition from Table 2, it was observed that the theoretically predicted \( q_e \) values increases with increasing initial dye concentration. However in the actual adsorption process, which is a surface phenomena, the amount of dye adsorbed should increase with increasing initial dye concentration. From Table 2, the reasonably higher \( r^2 \) values for type 5 expressions suggests that it can be used to represent the kinetics of methylene blue onto activated carbon. However the theoretically predicted \( q_e \) value using type 5 expressions suggests it is highly irrelevant to use a pseudo second-order model as it violates both the theory and the adsorption phenomena. Thus the theory behind the pseudo second-order model was getting valid for a type 1 pseudo second-order expression and the theory of pseudo second-order kinetics and the adsorption theory was found to getting vio-
lated by a type 5 pseudo second-order expression for the same experimental equilibrium data of methylene blue onto activated carbon. These two observations based on a type 1 and type 5 expressions suggests that the linear method just verify the hypothesis of linear regression instead of verifying the theory of adsorption kinetics. These different observations and predictions by linear method show the complexities in predicting the optimum sorption kinetics. These different outcomes 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 variation in the error structure will get varied upon linearizing the non-linear equation. The error distribution may vary the better or worse depending on the way the kinetic model is linearized.

This is because of the problem with the linear method as they cause some of the assumptions behind linear regression getting violated. The transformation of non-linear pseudo second-order expression to a type 3, type 4 and type 5 linear expressions distorts the experimental error. Linear regression assumes that the scatter of points around a line follows a Gaussian distribution and that the standard deviation is the same at every value of X. These assumptions are rarely true after transforming the experimental data. Sometimes these transformations alter the relation between Y and X. Say in the case of a type 1 pseudo second-order expression the kinetics of dye uptake process was found to fit the kinetic trend for the entire sorption period, i.e., the type 1 pseudo second-order expression well represents the multi-step sorption process or the kinetic trend is linear or not, instead it assumes the experimental data or the transformed experimental data are linear. The linear method does not check whether the process or the kinetic trend is linear or not, instead it assumes the experimental data or the transformed experimental data are linear. The linear method just verifies whether the transformed data or the experimental data are linear.

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In the present case, the pseudo second-order expression transforms to the best in case of type 1 linear form and the pseudo second-order expression transforms to the worse in case of type 5 linear expressions. Various outcomes for the five linearized equations are also due to the different axial settings due to the transformation of non-linear kinetic expression to various linear expressions (types 1–5). The various outcomes due to linearization process [18]. The linear method does not check whether the process or the kinetic trend is linear or not, instead it assumes the experimental data or the transformed experimental data are linear. The linear method just reports the slope and intercept for a linear trendline that best predicts the Y value for a given X. This makes the reason for the better or worse fit of pseudo second-order kinetics due to the various axial settings due to the transformation of non-linear kinetic expression to various linear expressions (types 1–5). The various outcomes due to linearization clearly indicates that for linear method, all the uncertainty is in Y, while X is known precisely. This confirms the possibility of the violation of the normality assumptions behind the linear regression method. Thus it will be more appropriate to use non-linear method to estimate the parameters involved in the kinetic rate expression. Also, non-linear method has an advantage that the error distribution does not get altered as in linear technique, as all the isotherm parameters are fixed in the same axis.

In the case of Lagergren pseudo first-order kinetics, the very lower \( r^2 \) value for a given \( K \) and \( q_e \) is applicable to computer operation, was developed and used to determine the kinetic parameters by minimizing the respect-
The coefficient of determination between experimental data and predicted values using the solver add-in with Microsoft’s spreadsheet, Microsoft Excel. Figs. 3 and 4 show experimental data and the predicted pseudo-second-order and pseudo-first-order kinetics using non-linear method. Figs. 3 and 4 also show the experimental kinetic data of methylene blue onto activated carbon. The obtained pseudo-first-order rate constant $K_1$, pseudo-second-order rate constant $K_2$, initial sorption rate $h$, and the predicted $q_e$ values by non-linear analysis were given in Table 3. From Table 3, the very higher $r^2$ values for a pseudo-first-order kinetics suggests this model can be used to represent the kinetic uptake of methylene blue onto activated carbon. While comparing the $r^2$ value of pseudo-first-order kinetics obtained by linear method (Table 2) and non-linear method (Table 3), it can be observed that the linear method fails to well represent the kinetics of methylene blue onto activated carbon. However the excellent fit of pseudo first-order kinetic in the experimental kinetic data for the entire sorption period suggests it is not appropriate to use the linear regression method while using the Lagergren pseudo-first-order kinetic expression. From Table 3, it was also observed that the pseudo-first-order kinetics predicts the $q_e$ value more accurately suggesting the applicability of this model in representing the methylene blue uptake by activated carbon particles at equilibrium conditions. The best and worse fit of experimental kinetic data in pseudo-first-order kinetics by non-linear and linear method suggests the kinetics is transforming to the worse while linearizing the non-linear pseudo-first-order kinetics expression. Thus it is inappropriate to use the Lagergren pseudo-first-order kinetic expression to check whether the experimental kinetic is following a first-order kinetics. Instead non-linear first-order expression would be a better option to check the applicability of pseudo-first-order kinetics with the experimental kinetic data. In the case of pseudo-second-order kinetics, by non-linear method, the results from the five pseudo-second-order kinetic linear equations are the same. By using non-linear method there are no problems with transformations of non-linear pseudo-second-order equation to linear forms, and also they are in the same error structures. Thus it

<table>
<thead>
<tr>
<th>$C_0$</th>
<th>Pseudo second-order kinetics (non-linear expression)</th>
<th>Pseudo first-order kinetics</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$</td>
<td>$K_2$</td>
<td>$q_e$</td>
</tr>
<tr>
<td>100</td>
<td>221.5</td>
<td>0.021366</td>
<td>221.0671</td>
</tr>
<tr>
<td>125</td>
<td>234</td>
<td>0.018162</td>
<td>235.4824</td>
</tr>
<tr>
<td>150</td>
<td>247</td>
<td>0.017884</td>
<td>248.476</td>
</tr>
<tr>
<td>175</td>
<td>268</td>
<td>0.014624</td>
<td>269.7243</td>
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<tr>
<td>200</td>
<td>286</td>
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<td>310</td>
<td>0.009587</td>
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</tr>
<tr>
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<td>332</td>
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<td>335.0096</td>
</tr>
<tr>
<td>275</td>
<td>364</td>
<td>0.008779</td>
<td>366.3623</td>
</tr>
</tbody>
</table>
will be more appropriate to use non-linear method to estimate the parameters involved in the kinetic equation. Also non-linear method had an advantage that the error distribution does not get altered as in linear technique, as all the kinetic parameters are fixed in the same axis.

As the present investigation confirms the non-linear method as an appropriate technique to predict the optimum sorption kinetics, the best-fit linearized form of pseudo second-order model was determined by comparing it with the constants predicted from the non-linear method. However a type 5 expression was omitted in the comparison study as it was found to violate the theory behind the pseudo second-order kinetics and also the adsorption theory. The effect of linearization on the kinetic parameters was estimated by plotting the $K_2$, initial sorption rate and predicted $q_e$ values calculated by non-linear method against these constants predicted by linear method as shown in Figs. 5–7, respectively. From Figs. 5–7, it was observed that the kinetic parameters obtained from Ho’s type-1 expression alone produced different observations, whereas the $K_2$ and initial sorption rate are more or less in a same trend line. A best fit linear expression does not depends only on how it best represent the experimental data, instead it should be accurate in predicting the rate kinetic parameters, which actually play a key role in adsorber design. From Figs. 5 and 6 it was observed that it is inappropriate to use the Ho pseudo second-order expression, instead the other three linearized forms of pseudo second-order expression, which show consistency in predicting the rate constant $K_2$ and the initial sorption rate. However from Fig. 7, it was clear that Ho’s type 1 pseudo second-order expression provides good correlation with non-linear method in predicting $q_e$ (mg/g), the amount of dye adsorbed at equilibrium condition.

The relation between initial sorption rate $h$ (mg/g min) and the rate constant $K_2$ (g/mg min) predicted by non-linear method with $C_0$ is given by Eqs. (7) and (8) with a correlation coefficient of 0.9755 and 0.9615, respectively:

$$K_2 = \frac{C_0}{155.39C_0 - 13438}$$  \hspace{1cm} (7)

$$h = \frac{C_2}{0.3297C_0 - 26.592}$$  \hspace{1cm} (8)

As the present study shows that it is inappropriate to use Ho expression in predicting the sorption kinetics, it is better to avoid using the Ho kinetic expression, instead the remaining the three other alternate linearized forms (Table 1) can be used to explain the methylene blue/activated carbon system.

![Fig. 5. Effect of linearization on initial sorption rate, $h$.](image1)

![Fig. 6. Effect of linearization on pseudo second-order rate constant, $K_2$.](image2)

![Fig. 7. Effect of linearization on the amount of dye adsorbed (predicted $q_e$).](image3)
4. Conclusions

The sorption of methylene blue onto activated carbon was found to be well represented by the pseudo first-order and pseudo second-order kinetics. The present study confirms it is highly irrelevant to use linear method to obtain the parameters in Lagergren pseudo first-order kinetic expression. By linear method a type 1 expression very well represent the kinetic uptake of methylene blue onto activated carbon. A type 5 expression was found to be the worse fit pseudo second-order kinetic expression. Non-linear method was found to be a better method than the linear method for predicting the optimum kinetics and the parameters involved in them. By non-linear method both pseudo first-order and pseudo second-order kinetics very well represent the kinetics of methylene blue onto activated carbon. Non-linear method is the correct way to obtain the parameters involved in the pseudo first-order kinetics. The types 2–4 pseudo second-order expressions produced similar second-order kinetic constants similar to that of non-linear pseudo second-order kinetics.

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References