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Comparative Analysis of Different Linearized Expressions of Estimating the Pseudo-Second-Order Kinetic Parameters for the Adsorption of Methylene Blue on Hydrochloric Acid-Treated Rice Husk

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Abstract- A comparison between six different types of linear expression of the widely usedpseudo-second-order kinetic model, for the adsorptionofmethylene blueon hydrochloric acid-treated rice huskwas made. The results showed that it was inappropriate to use the type 1 expression of pseudo-second-order equation to calculate the pseudo-second-order rate constantsand to predict q_t for the studied system, even the type 1 expression had high R^2 value. The modeling of kinetic results showed that the studied system (methylene blue/hydrochloric acid-treated rice husk) was best described by the type 6 expressionof the pseudo-second-order equation

Index Terms- Linear regression; Pseudo-second-order; hydrochloric acid-treatedrice husk; Adsorption; Methylene blue; Kinetics

I. Introduction

Elimination of dye pollutants in handling of waste water has long been considered. The most frequently used procedures for elimination of dye are biological, physical or chemical methods (Shih 2012). All these methods have diverse dye elimination abilities, principal expenses, and operating rates. Adsorption referred to the passive uptake and physic chemical binding of dye to the adsorb ate surface,is now broadly recognizedasaneffectiveandeconomicallyfeasibleprocedureforthe eliminationofdyepollutants fromwastewaters(Chowdhury and Das Saha 2011). So the adsorption research is of great significance for getting maximum elimination of dye pollutants. Theadsorptionkinetic modelsilluminatetheuptakerateofadsorbate, whichcan be usedto predicttheadsorptionmechanism.Therefore,an broadinvestigationof adsorptionkinetic models is important. Numerousadsorptionkineticmodelsare established toexplicate the reaction order ofadsorption systems on the basis of solution concentration(Chowdhury and Das Saha 2011).The pseudo-second-orderkineticmodelis themostrecognizedmodel inmostadsorptionkineticresearchsandhavebeen commonlyappliedtodescribe time evolution of adsorption under nonequilibrium conditions (Ho, Ng et al. 2000). In most suitcases, the pseudo-second-order model can be done by using some altered equations that have been established over the past few decades. Among these formulations, Ho’s equation has been intensively used to test for the correlation of the adsorption data for pseudo-second-order kinetic model during the past decade due to its simplicity and its good fitting of many adsorption systems(Shahwan 2014).Because the form of pseudo-second-order as expressed in literatures is nonlinear, the non-linear regression method was utilizedto evaluate the values of q_e and K_2 requires for fitting the equation to experimental data(El-Khaiary, Malash et al. 2010). The calculation of pseudo-second-order equations by using the non-linear regression method presentsa more difficultcalculated processfor determining equation parameters and the scientists need to use some specific softwares or write dwown some computer programs to solve the non-linear regression equation. Owing to these reasons, the rsearchers attempt to gaina simpleway to solve the pseudo-second-order eqauation. A conventioanl alternative technique is to use linearized forms of the pseudo-second-order equation to replace non-linear form of the pseudo-second-order equation to compute the two parameters, q_e and K_2. This linear regression method is commonly employedto predictthe pseudo-second-order parameters, since this method only involves slight understanding of the data fittingprocess, and is easily solvedby using Excel or similar spreadsheet softwares(El-Khaiary, Malash et al. 2010).However, depending on the method of the pseudo-second-order equation linearized, the error distribution may shift worse. Thus it will become an inappropriate alternative approach to use the linearization process toassessthe pseudo-second-order parameters.

In this study, 6 different types of linear expressions of the pseudo-second-order kinetic equations has been appliedtocalculatethe kinetic parameters and also to find the best linear type on the basis of the experiment data.

II. Materials and Methods

The experimental data utilizedin this research was obtainedfrom the literature (Shih 2012). The adsorbent utilizedin the literature washydrochloric acid-treated rice husk (HRH) and the dye utilizedin the literature was methylene blue (MB). The amount of dye adsorbed at time t (q_t) and the amount of dye adsorbed at equilibrium time (q_e), is computedby the following equations (Djeribi and Hamdaoui 2008, Huang and Shih 2014):

Amount adsorbedat time t (q_t) = $\frac{(C_i - C_t)V}{M}$ (1)

Amount adsorbed at equilibrium time (q_e) = $\frac{(C_i - C_e)V}{M}$ (2)

where V is the volume of dye solution (L).C_i, C_t and C_e(mg/L) are the liquid phase concentrations of dyes initially, at time t and at equilibrium time, respectively.M is the weight of adsorbent used (g).

The differential form of pseudo-second-order equation derived on the basis of adsorption capacity on solid phase can be written as follows (Ho, McKay et al. 2000, Demirbas, Kobya et al. 2004, Ofomaja 2007, Sari, Tuzen et al. 2007, Neşe and T. Ennil 2008):

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (3)$$

where q_t(mg/g) is the amount of MB sorbed on the surface of HRH at time t (min); q_e is the amount of MB sorbed at equilibrium (mg/g) and K_2, the rate constant of the sorption (min^{-1}). Integrating Eq. [3] for the boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t gives(Huang and Shih 2014):

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t \quad \text{type1} \quad (4)$$

which is thelinearized forms of the integrated rate law for the pseudo-second-order equation.Eq.[4] will be the first type of linearized forms of pseudo-second-order equation. Eq.[4] can be rearranged to obtain another 5 alternativelinearized types of pseudo-second-order expressions(Kumar 2006, Hamdaoui, Saoudi et al. 2008, Chowdhury and Das Saha 2011):

$$\left(\frac{1}{q_t}\right) = \frac{1}{q_e} + \frac{1}{K_2 q_e^{\,2}}\frac{1}{t} \quad \text{type2} \quad (5)$$

$$q_t = q_e - \frac{1}{K_2 q_e}\frac{q_t}{t} \quad \text{type3} \quad (6)$$

$$\left(\frac{q_t}{t}\right) = K_2 q_e^{\,2} - K_2 q_e q_t \quad \text{type4} \quad (7)$$

$$\left(\frac{1}{t}\right) = -K_2 q_e + K_2 q_e^{\,2}\frac{1}{q_t} \quad \text{type5} \quad (8)$$

$$\left(\frac{t}{q_t}\right) = \frac{1}{K_2 q_e^{\,2}} + \frac{1}{q_e}(t) \quad \text{type6} \quad (9)$$

III. Results and Discussion

Linear regression is frequently applied to find the best-fitting kinetical equation. For the present study, the experimental data for MB adsorbed onto HRH were fitted to the six different linearized forms of pseudo-second-order equations. The theoreticalq_e andthe rate $K_2$for the type 1 linearized forms of pseudo-second-order expression can be obtained from the slope and intercept of the plots between 1/(qe-q_t) and t (fig.1). In fact, the rate constant K_2 and the theoretical q_e for the various linearized form of pseudo-second-order equations, i.e., type 2, type 3, type 4, type 5 and type 6 also can be calculated from the plot of 1/$q_t$vs. 1/t (fig.2), q_t vs. q_t/t(fig.3), q_t/t vs. q_t (fig.4),1/t vs. 1/ q_t (fig.5) and t/ $q_t$vs. t (fig.6), respectively(Kumar 2006, Hamdaoui, Saoudi et al. 2008).

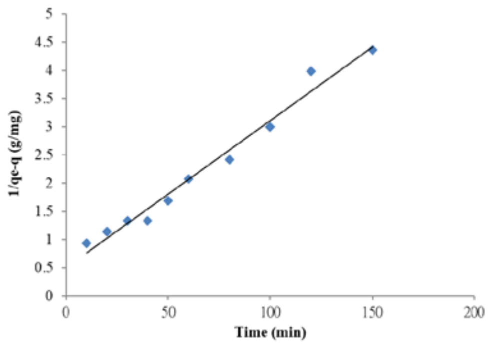

Figure 1. Type 1 pseudo-second-order equation obtained using linear method for the sorption of MB onto HRH

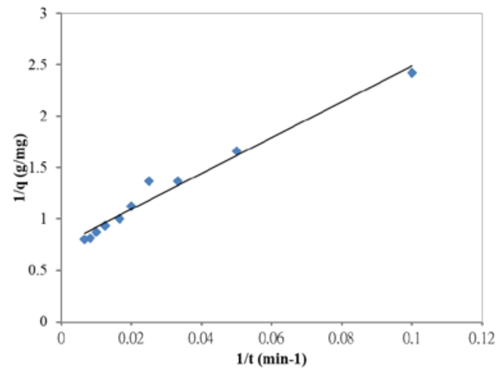

Figure 2. Type 2 pseudo-second-order equation obtained using linear method for the sorption of MB onto HRH

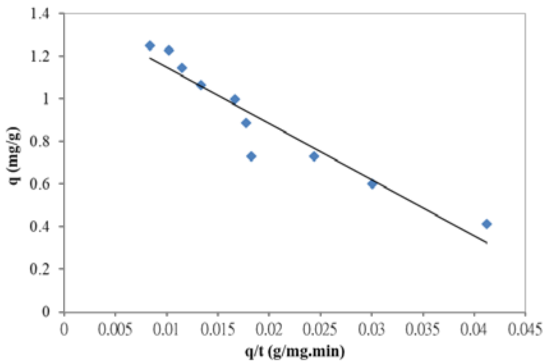

Figure 3. Type 3 pseudo-second-order equation obtained using linear method for the sorption MB onto HRH

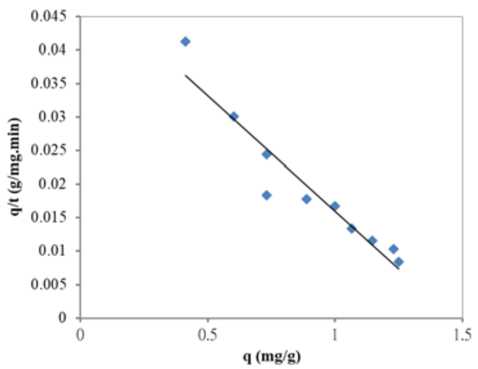

Figure 4. Type 4 pseudo-second-order equation obtained using linear method for the sorption of MB onto HRH

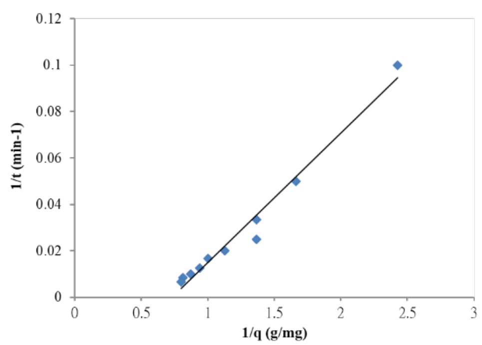

Figure 5. Type 5 pseudo-second-order equation obtained using linear method for the sorption of MB onto HRH

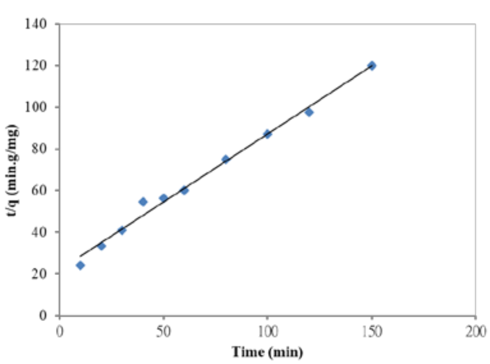

Figure 6. Type 6 pseudo-second-order equation obtained using linear method for the sorption of MB onto HRH

The best-fit linear form of kinetic equations is generally selected based on the error functions that produce minimum error distribution between the experimental and predicted values.The calculatedresults of kinetic parameters and the correlation coefficient, R^2 for these 6 different linearized types of pseudo-second-order equationsareshown in table 1. It was observed that theq_e values, K_2 values and R^2valuescalculatedfrom thesix linear expressions of pseudo-second-order equations were different.From table 1, it can be observed that different linear expressions of the same kinetic model significantly affect calculations of the parameters. Also, it was observed thattype 6 expression hadthe highest R^2 value (0.9905) for the MB adsorption on HRH, this high R^2 value impliedthat Type 6 linear expression of pseudo-second-order

Linear Type	qe (mg/g)	K2(g/mg.min)	R2
Type1	1.962	0.026	0.9788
Type2	1.344	0.0317	0.9748
Type3	1.4108	0.02689	0.9084
Type4	1.46087	0.0236	0.9084
Type5	1.3676	0.0298	0.9748
Type6	1.53	0.0196	0.9905

equatuion would be the most suitable for theexperimental results ofthe MB adsorption on HRH. From table 1, it was observed that the R^2 values of type 3 and type 4 expressions are lower than 0.91, and the R^2 values of type 1, type 2 and type 5 expressions are higher than 0.97. These high R^2 values of type 1, type 2 and type 5 expressions indicated that these three type linear expressions may also be used to represent the MB adsorption on HRH.From table 1, the q_e values predicted by type 6and type 4 linear expressions closely relate with experimental value. However, from table 1, it was able to be observed that the type 1, type 2 and type 5expressions of pseudo-second-order equation failed to predict the q_e values theoretically. In order to provethe precisionof the$q_t$calculatedby these 6 different linearized types of pseudo-second-order equation. The q_e valuesand$k2$ valuesobtained from these six linear types of pseudo-second-order equations were bring into the nonlinear form of pseudo-second-order equation to compute the q_t valuses. The nonlinear form of pseudo-second-order equation appliedhere is expressed as followed (Kumar 2006):

$$q_t = \left(\frac{K_2 q_e{}^2 t}{1 + K_2 q_e t} \right) \quad (10)$$

Comparison between the experimental points and predicted q_t for the adsorption of MB onto HRH by these six linear expressions of pseudo-second-order expressions were showedin figure 7-12. If theR^2 values were used for comparison, the Type 6 linear expression would be most suitable, followed by the Type 1 linear expression. However, compared with the predicted$q_t$value of the Type 1 linear expression, the predicted q_t of the Type1 linear expression was greatly deviated from the experimental points. The figure 12 indicated that thetype 6linear expression of pseudo-second-order equatuionsucceed to predict the q_t for the adsorption of MB onto HRH.All these

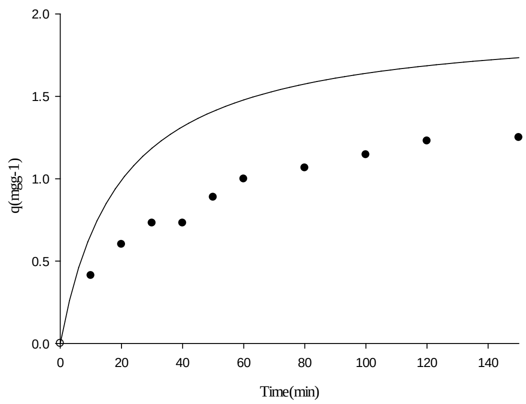

Fig. 7. Comparison between the experimental points and predicted qt for the adsorption of MB onto HRH by linear type 1.

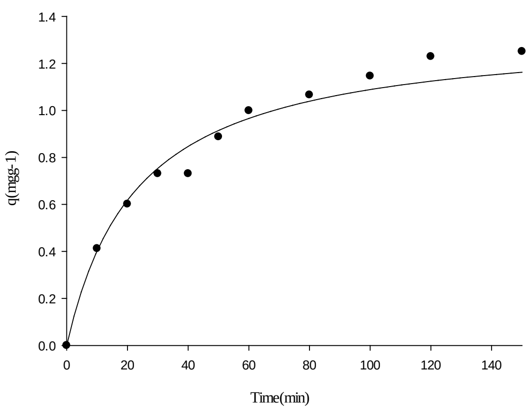

Fig. 8. Comparison between the experimental points and predicted qt for the adsorption of MB onto HRH by linear type 2.

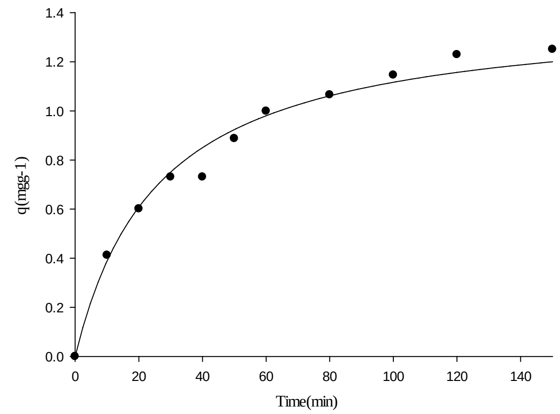

Fig. 9. Comparison between the experimental points and predicted qt for the adsorption of MB onto HRH by linear type 3.

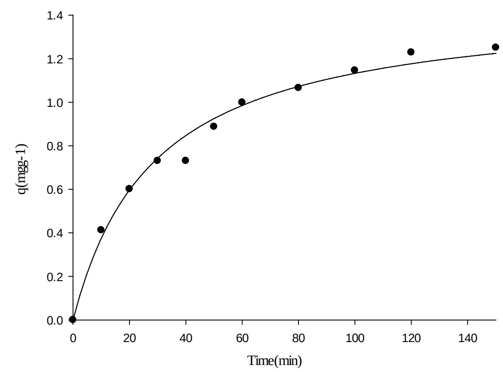

Fig. 10. Comparison between the experimental points and predicted qt for the adsorption of MB onto HRH by linear type 4.

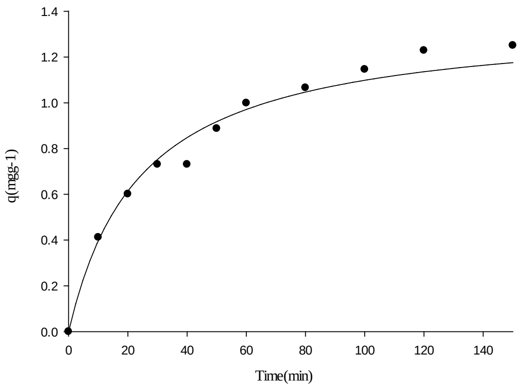

Fig. 11. Comparison between the experimental points and predicted qt for the adsorption of MB onto HRH by linear type 5.

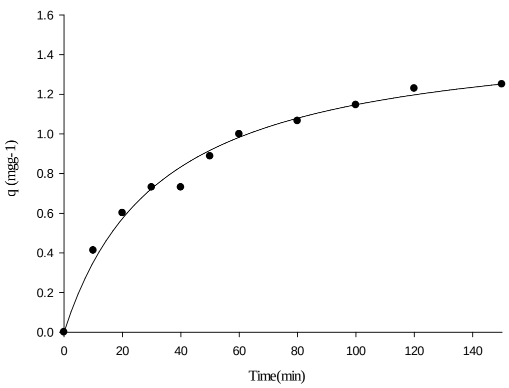

Fig. 12. Comparison between the experimental points and predicted qt for the adsorption of MB onto HRH by linear type 6.

outcomesindicated that the hypothesisbehind the pseudo-econd-order kinetics was becomingvalid for the adsorption of MB onto HRH based on the type 6 linear expression and the hypothesisbehind the pseudo-second-order kinetics was disobeyedby the type 1 linear expression.These outcomes also showed that variouslinear formsof the same pseudo-second-order kinetic equatuionssignificantly influencethe calculations of the parameters.The different axis setting of the different linear expression could change the regression results, thereby influencing the consistency as well asaccuracy. Also, the divergent outcomes of different linearized form of pseudo-secondorder equatuionscould be caused by the variation in the error structure that would get varied upon the transformation of a nonlinear expression to a linear expression(Khambhaty, Mody et al. 2008). These observations point outthatthe error distribution might modifyto worse or better depending on the expression of the pseudo-secondorder kinetic equatuion is linearized. This was because of the problem with the linearizationtechnique as they cause numerousassumptions behind the linear regression becominginfringed(Khambhaty, Mody et al. 2008). From these figures, it was observed that the linear expressions of type 4 and type 6 can predict the experimental data very well.

IV. Conclusion

From the survy of literatures, it can be found that the linear technique has been commonly appliedin evaluatingthe quality of fit of a kinetic model to an experimental data in most adsorption researches. However, the transformation of a nonlinear expression to a linear expression could alterthe normality assumptions of the linear least square method. A comparative investigation of six different linear expressions of pseudo-second-order equations in determining the kinetic parameters was conducted. The present findings suggest that it is not appropriate to use the R^2 values to select the best-fit linear forms of the same pseudo-second-order kinetic equatuion. The present findings suggest that the figures of comparison between the experimental points and predicted $q_t$values which were calculated by the q_e valuesand$k2$ valuesobtained from these six linear types of pseudo-second-order equations can be used to determine the best-fitting linear expression of the pseudo-second-orderequatuion.

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