Application of Excel Spreadsheet for comparative analysis of linearized expressions of kinetics modelling for the adsorption of methylene blue on rice husk

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Abstract- In order to explore the feasibility of six different linear conversion methods applied to nonlinear pseudo-second-order kinetic equations, six linear expressions are derived from these different conversion methods. These linear expressions are applied to the experimental data and used the mathematical and statistical data obtained from the calculation of these 6 linear expressions to analyze and determine which linear expression calculated the data closest to the actual experimental data than the other linear expressions. Most computers are equipped with EXCEL, so it is the most suitable tool for researchers to apply the EXCEL on these linear equations for various calculations and statistical analysis. Therefore, the *Data Analysis toolpak*, an analysis tool incorporated into Microsoft Excel for Windows, was used to analyze and find the best linear type fitted to experimental data from 6 different types of linear expression of pseudo-second-order kinetic equation.

Index Terms- Pseudo-second-order; Adsorption; Kinetics; Excel

I. Introduction

Humans have a long history of using dyes. Most raw materials for dyes come from natural minerals and plants. Due to the limited amount of some of these raw materials, they cannot be obtained in large quantities, so that the use of some dyes cannot be applied to daily life in large quantities. Since the first dye was synthesized in the nineteenth century, humans have successively synthesized more than 1,000 kinds of artificial chemical dyes. These dyes that can be manufactured by a large number of industrializations have popularized the application of dyes. Compared to natural dyes, these artificial dyes are difficult to decompose by microorganisms. Therefore, when humans manufacture and use these dyes in large quantities, the wastewater containing dyes in these factories is released into the environment. With the increasing use of dyes by human beings, it is an important issue to remove these dyes from wastewater to reduce the pollution of dye wastewater to the environment. There are many techniques that can be used to remove dye from wastewater. Most of these technologies use physical removal processes, chemical removal processes, or biological removal processes to remove dyes from wastewater. (Shih 2012). One of the more commonly used dye removal methods is the adsorption method (Chowdhury and Das Saha 2011). Many scientists who study the use of adsorption to remove dyes try to explore how to achieve the maximum efficiency of adsorption. In these studies, some researchers tried to explore the mechanism of adsorption by using adsorption kinetics. Many adsorption kinetic models based on solution concentration are applied to explore the adsorption mechanism. Among these adsorption kinetic models, the pseudo-second-order kinetic model is the most commonly used to describe time evolution of adsorption under nonequilibrium conditions (Ho, Ng et al. 2000). Ho 's formulation is the most widely used equation in the expression of pseudo-second-order kinetic model in adsorption research due to its simplicity and its good fitting of many adsorption systems (Shahwan 2014). The pseudo-second-order kinetic equation is a nonlinear mathematical equation. In order to reduce the difficulty of applying nonlinear equations, many researchers use different linearization conversion methods to convert this nonlinear equation into a linear equation to calculate the two parameters, q_e and K_2. This linear regression method only requires little understanding of the data fitting procedure, and is easily done by using Excel or similar spreadsheet software(El-Khaiary, Malash et al. 2010). However, some linear equations may make the error distribution worse. Thus, it will become an unsuitable alternative method to use the linearization process to estimate the pseudo-second-order parameters. Also, there are a lot of software that can be used to calculate these linear equations, and can convert these data into graphs. The most popular of software is Microsoft's EXCEL. In this discussion, EXCEL will be used to calculate the parameters in the linear equation and perform statistical analysis.

In this study, statistical analysis with Excel was applied on 6 different types of linear expressions of the pseudo-second-order kinetic equations to analyze the statistical results of these 6 different linear types on the basis of the experiment of methylene blue adsorption from its aqueous solution onto rice husk.

II. Materials and methods

The data in this study comes from this literature (Huang and Shih 2015). In the experiment, rice husk (RH) was used as an adsorbent, and the dye used in the experiment 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), are calculated using 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).

2.1. The pseudo- second-order kinetic model

The differential equation of pseudo-second-order kinetic model derived on the basis of sorption capacity on solid phase is expressed as follow (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 adsorption at time t (min); q_e is the amount of adsorption at equilibrium (mg/g) and K_2, the rate constant of the pseudo-second-order equation (min^{-1}). Equation 3 is integrated under the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$ to obtain the following equation (Huang and Shih 2014):

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

Eq. [4] will be the first type of linearized forms of pseudo-second-order expression. Eq.[4] undergoes different linear transformations and arrangements to obtain another five linear expressions of the pseudo-second-order equation (Kumar 2006, Hamdaoui, Saoudi et al. 2008):

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

$$q_t = q_e - \frac{1}{K_2 q_e^{\,2}}\frac{q_t}{t} \quad \text{type3} \quad (6)$$

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

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

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

III. Results and Discussion

For the present study, the experimental data were fitted to the 6 different linearized forms of pseudo-second-order expression described above and analyzed by the Data Analysis Toolpak in Excel. Values of regression statistics were presented in table1. From table1, it can be found that the multiple R value of types 6 is closer to 1 than the multiple R value of other five linear types. These results indicated that the data clusters of linear types of 6 is around the regression line. Similarly, from table1, it can be found that the R^2 value of type 6 is closer to 1 than the R^2 values of other five linear types. The highest R^2 values of types 6 make it to be the best linear expressions of pseudo-second-order equation among these six pseudo-second-order equations. The standard error of the regression, also recognized as the standard error of the estimate, and the value of *standard error* is used to evaluate the standard deviation about the regression.

Table1: Regression Statistics for

	type1	*type 2*	*type 3*	*type 4*	*type 5*	*Type6*
Multiple R	0.9837974	0.9966827	0.9935584	0.9935584	0.9966827	0.9998588
R Square	0.9678573	0.9933764	0.9871583	0.9871583	0.9933764	0.9997176
Adjusted R Square	0.9638395	0.9925485	0.985553	0.985553	0.9925485	0.9996823
Standard Error	0.5380553	0.0065583	0.0321573	0.0049102	0.002459	0.3341108
Observations	10	10	10	10	10	10

Table 2 is the analysis results of variance (ANOVA) table. In table 2, the output values of Significance F indicate the probability that the regression output could have been obtained by chance. A small value of Significance of F suggests that there is solid evidence for accepting the regression model. In table 2, the Significance F values of these 6 different linear expressions are all less than 0.05, and these low Significance F values show that these 6 different linear expressions was not a chance occurrence.

Table 2: ANOVA

Type1					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	69.738609	69.738609	240.89034	2.957E-07
Residual	8	2.3160284	0.2895036		
Total	9	72.054637			
Type 2					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.0516049	0.0516049	1199.8114	5.277E-10
Residual	8	0.0003441	4.301E-05		
Total	9	0.051949			
Type 3					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.6359329	0.6359329	614.96838	7.475E-09
Residual	8	0.0082727	0.0010341		
Total	9	0.6442057			
Type 4					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.0148267	0.0148267	614.96838	7.475E-09
Residual	8	0.0001929	2.411E-05		
Total	9	0.0150196			
Type 5					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.007255	0.007255	1199.8114	5.277E-10
Residual	8	4.837E-05	6.047E-06		
Total	9	0.0073034			
Type 6					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	3161.8853	3161.8853	28324.676	1.738E-15
Residual	8	0.8930405	0.1116301		
Total	9	3162.7783			

Using these 6 different linear equations to analyze and calculate the experimental data, some of the results are summarized in table 3. From the P-value data of table 3, we can find that the P-value of these 6 linear equations are all less than 0.05. This phenomenon means that these tests are statistically significant. In other words, these 6 linear types are acceptable to simulate the adsorption of MB by using RH.

Table 3: The values for the model's coefficients

Type1								
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	0.2458161	0.3096555	0.7938374	0.450193	-0.468251	0.959883	-0.468251	0.959883
X Variable 1(t)	0.060841	0.00392	15.520642	2.957E-07	0.0518014	0.0698805	0.0518014	0.0698805
Type 2								
Intercept	0.4152216	0.0030002	138.39957	8.308E-15	0.4083032	0.42214	0.4083032	0.42214
X Variable 1 (1/t)	2.6581702	0.0767408	34.638294	5.277E-10	2.4812056	2.8351348	2.4812056	2.8351348
Type 3								
Intercept	2.4144728	0.0170057	141.98017	6.773E-15	2.3752575	2.453688	2.3752575	2.453688
X Variable 1 (q/t)	-6.506937	0.2623918	-24.79856	7.475E-09	-7.112013	-5.90186	-7.112013	-5.90186
Type 4								
Intercept	0.3669634	0.0127976	28.674425	2.367E-09	0.3374521	0.3964746	0.3374521	0.3964746
X Variable 1 (q)	-0.151709	0.0061176	-24.79856	7.475E-09	-0.165816	-0.137601	-0.165816	-0.137601
Type 5								
Intercept	-0.154984	0.0053468	-28.98645	2.172E-09	-0.167314	-0.142654	-0.167314	-0.142654
X Variable 1 (1/q)	0.3737069	0.0107888	34.638294	5.277E-10	0.3488278	0.398586	0.3488278	0.398586
Type6								
Intercept	2.9271162	0.1922837	15.222905	3.437E-07	2.4837092	3.3705231	2.4837092	3.3705231
X Variable 1 (t)	0.4096685	0.0024342	168.29936	1.738E-15	0.4040553	0.4152817	0.4040553	0.4152817

When using EXCEL's Data Analysis Toolpak to analyze data, the Data Analysis Toolpak provides Residual Plot, Line Fit Plot, and Normal Probability Plot. The Residual Plots of these 6 linear types were presented in figure 1a-1f. The Line Fit Plots of these 6 linear types were presented in figure 2a-2f. We can use the residual plot to estimate whether the observed or predicted error (residual residuals) is consistent with the random error (stochastic error). If the point distribution on the residual plot is randomly scattered on the horizontal axis, it means that the value obtained by this linear equation can be reasonably compared with the experimental data. Conversely, if the point distribution on the residual plot is not scattered on the horizontal axis, it means that this linear equation is not suitable for calculating data comparable to the experimental data.t From the fig 1a to fig 1f, we can find these scatter plots displays a fairly random pattern.. This random pattern shows that these 6 linear type expressions offer a decent fit to the experimental data. These figures suggest that the transformation of 6 linear types to achieve linearity were successful. Also, the residual distribution pattern of the linear type 6 were smaller than the other 5 linear types, it indicated that the transformed data of linear type 6 resulted in a better model.

Figure1a. Residual Plot

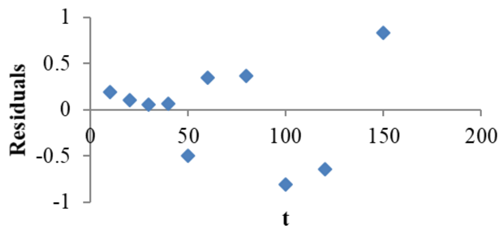


Figure1b.Residual Plot

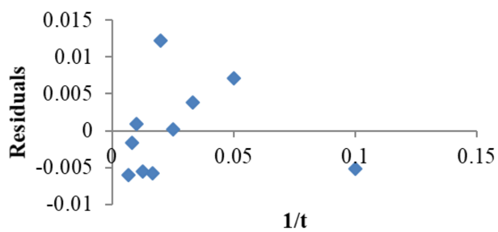


Figure1c.Residual Plot

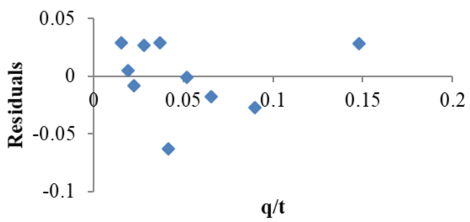


Figure1d. Residual Plot

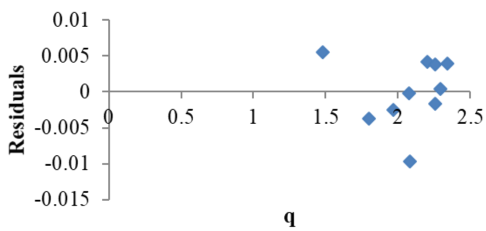


Figure1e.Residual Plot

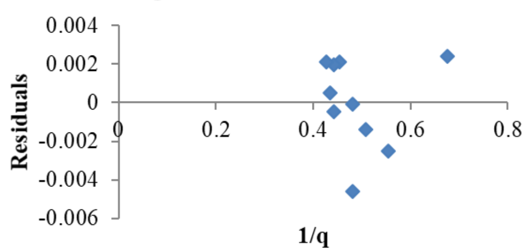
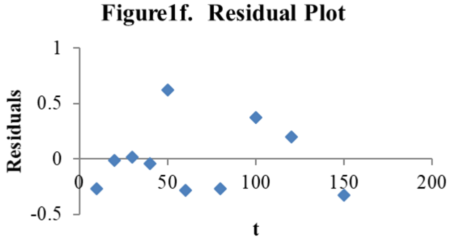


Figure1f. Residual Plot



The fig 2a-f is a comparison chart between the data calculated by six different linear expressions and the experimental data. From the comparison chart, it can be understood which linear expression can more accurately calculate the calculation that is consistent with the actual experimental data. value. From fig 2a-f, it can be found that the data calculated by these six different linear expressions are quite consistent with the experimental data. Such results show that these six linear conversion methods can be successfully applied to the linearization of nonlinear pseudo-second-order equations.

Figure2a. Line Fit Plot

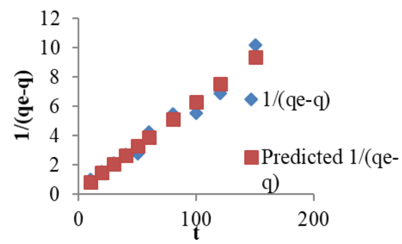


Figure2b. Line Fit Plot

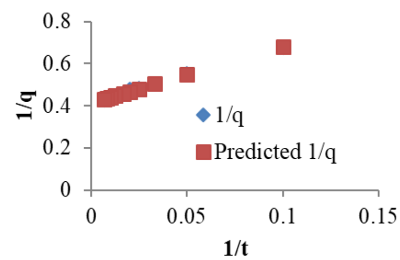


Figure2c. Line Fit Plot

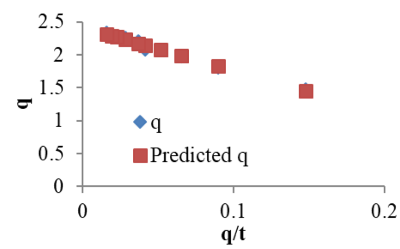
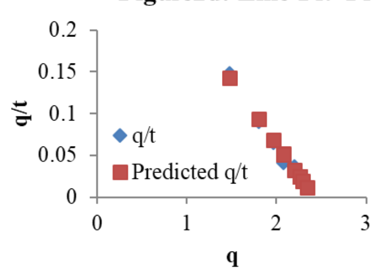
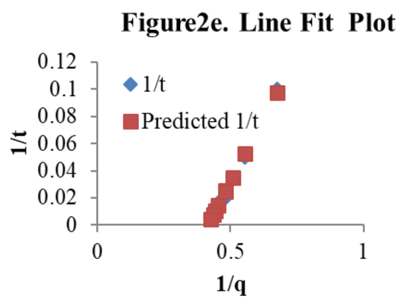
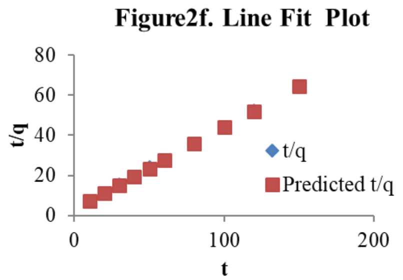


Figure2d. Line Fit Plot







However, from fig 2a-f, we can still find that the 2 linear expression and the 6 linear expression can calculate the value more accurately than the other four linear expressions.

IV. CONCLUSION

In this study, a nonlinear pseudo-second-order equation was used to analyze and calculate the value of adsorption. However, the non-linear expression method often causes computational problems and increases the difficulty of applying it to simulation calculations. In this study, 6 different linear conversion methods were applied to this nonlinear pseudo-second-order equation and converted into 6 different linear equations. In order to explore which of the six different linear expressions can more accurately calculate the required value. Therefore, EXCEL, which is equipped with computers, is used for analysis and discussion to find out which linear expression is more accurate. The data analysis toolpak of excel were applied to analyze the different linear types. From the *Regression Statistics* tables and ANOVA table, the output obtained from the data analysis toolpak by using these 6 linear expressions of pseudo-second-second equation indicate that the best-fit linear types is linear type 6. In fact, the good predictive values are still available for most of the experimental data of these 6 expressions of pseudo-second-second equation. Compared with the difficulty of calculation caused by nonlinearity, linearizing nonlinear equations can indeed reduce the difficulty of calculation. This study also found that EXCEL's data analysis toolpak can indeed help researchers to judge the accuracy of linearized equations applied to data simulation.

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