Application of the Analysis *ToolPak* for comparison of various linearized expressions of kinetics equations for sorption of methylene blue onto nitric acid-treated rice husk

Yu-Ting Huang[1], Ming-Cheng Shih[2*]

[1]. Department of Nutrition, I-Shou University. No.8, Yida Rd., Jiaosu Village, Yanchao District, Kaohsiung City 82445, Taiwan, R.O.C.
[2]. Department of Biological Science and Technology, I-Shou University. No.8, Yida Rd., Jiaosu Village, Yanchao District, Kaohsiung City 82445, Taiwan, R.O.C.

DOI: 10.29322/IJSRP.11.06.2021.p11490
http://dx.doi.org/10.29322/IJSRP.11.06.2021.p11490

Abstract- Artificial dyes have been used for more than a hundred years, and there are many kinds of artificial dyes, so the application range is quite wide, such as textile industry, medicine industry, etc. However, artificial dyes are not easily decomposed by microorganisms and some dyes are toxic. Therefore, with the large-scale use of artificial dyes, the wastewater discharged from the factory will cause water environmental pollution if it is not treated. The adsorption method is currently a cheaper and more commonly used method. In order to obtain better adsorption efficiency, researchers have used different kinetic equations to study the adsorption mechanism. The data in this study meets the nonlinear pseudo-second-order kinetic equations. However, the nonlinear equations increase the difficulty of calculation and simulation. Therefore, many researchers convert this nonlinear equation through the linearization process into 6 different linear equations. In this study, the Analysis ToolPak in EXCEL was used to analyze the six different forms of linear equations to calculate the estimating value of sorption of methylene blue onto nitric acid-treated rice husk. The analysis results indicated that these linear equations can be applied to calculate accurate prediction values. However, the second type of linear equation can obtain more accurate prediction values than the other five equations.

Index Terms- Pseudo-second-order; Adsorption; Kinetics; Excel; nitric acid-treated rice hus

I. Introduction

Humans have a long history of using natural dyes such as vegetable dyes or mineral dyes to color clothes. However, due to the limited production of natural dyes and the instability of dyeing, users have not been popularized. This dilemma was not improved until the first artificial dye was developed. Subsequently, more than a thousand various artificial dyes have been synthesized. These artificial dyes are not only cheap, in addition to being used for dyeing clothes, but also used in medicine, food, etc. Artificial dyes also have great disadvantages. They are not easily decomposed by microorganisms like natural dyes, and they are also more toxic than natural dyes. Therefore, when artificial dyes are widely used in various industries, these industries will produce a large amount of colored wastewater. If these colored wastewaters are directly discharged into natural waters without treatment, it will cause great pollution to the environment. Therefore, some treatment methods for removing color materials in colored wastewater have been developed, and the more commonly used method is adsorption (Xiao, Jiang et al. 2020). In order to obtain better adsorption efficiency, many scientists have deduced many adsorption kinetics to study the adsorption mechanism. In previous studies, it was found that the model based on pseudo-second-order kinetic equation is the most suitable kinetic model. The pseudo-second-order kinetic model was derived by Ho and McKay(Ho and McKay 1998). This equation was originally a nonlinear equation. Many researchers convert this nonlinear equation into a variety of diverse forms of linear equations. (Huang, Lee et al. 2018). These diverse forms of linear equations can use EXCEL or some mathematical software to draw graphics and obtain some data. (Huang, Lee et al. 2018). These diverse forms of linear equations can use EXCEL or some mathematical software to draw graphics and obtain some data. (El-Khaiary, Malash et al. 2010).

The analysis toolpak in EXCEL can provide more analysis data to determine which linear conversion is more accurate. In this study, the analysis toolpak was applied on 6 diverse linear types of the pseudo-second-order kinetic equation to study the statistical outcomes on the basis of the experiment data of sorption of methylene blue (MB) onto nitric acid-treated rice Husk (NRH).

II. Materials and Methods

The experimental data used in this research was obtained from this literature (Huang, Lee et al. 2018). In this experiment, MB was used as dye, and NRH was used as an adsorbent. The amount of MB adsorbed at time t (q_t, mgg^{-1}) and the amount of MB adsorbed at equilibrium time (q_e, mgg^{-1}), are estimated utilizing the following equations (Huang and Shih 2020):

Amount adsorbed at 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 C_i, C_t and C_e (mg/L) are the concentrations of MB initially, at time t and at equilibrium time, respectively. V is the volume of MB solution (L). M is the weight of NRH used (g).

2.1. The pseudo-second-order kinetic equations

The original equation of pseudo-second-order kinetic equation obtained on the basis of sorption capacity on solid phase is a differential equation and expressed as follow (Ho and McKay 1998):

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

K_2 is the rate constant of the pseudo-second-order equation (gmg^{-1}min^{-1}). Eq. [3] is integrated under the boundary conditions q_t = 0 to q_t = q_t and t = 0 to t = t and undergoes diverse linear transformations and arrangements to become as follow 6 expressions (Ho and McKay 1998, Huang and Shih 2020):

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

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

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

$$\left(\frac{1}{q_t}\right) = \frac{1}{q_e} + \frac{1}{K_2 q_e^{\ 2}} \frac{1}{t} \quad \text{type4} \quad (7)$$

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

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

III. Results and Discussion

In this study, the experimental data of NRH adsorption of MB used the Analysis Toolpak in Excel to analyze the results obtained by applying the experimental data to 6 different linear equations. Table 1 is the analysis results of regression statistics table, and the results indicated that some of the multiple R value of obtained from six linear types of pseudo-second-order equations were different. The value of multiple R of type2 is closer to 1 than the values of multiple R of other five linear types. The value of R^2 of type 6 is closer to 1 than the values of R^2 of other five linear types. The highest multiple R value and highest R^2 values of types 2 indicated type2 is the best linear expressions of pseudo-second-order equation.

Table1: Regression Statistics

	type1	*type 2*	*type 3*	*type 4*	*type 5*	*Type6*
Multiple R	0.9863	0.9934	0.9765	0.9765	0.9286	0.9286
R Square	0.9729	0.9868	0.9536	0.9536	0.8622	0.8622
Adjusted R Square	0.9695	0.9851	0.9478	0.9478	0.8450	0.8450
Standard Error	0.1490	3.4704	0.0065	0.0913	0.1131	0.0049
Observations	10	10	10	10	10	10

Values of variance (ANOVA) were given in table2 and table 3. The Significance F values of these six different linear expressions in table 2 are all less than 0.05, these low values indicated that these 6 different linear expressions was not a chance occurrence. The P-values of these 6 linear equations in table 3 are all less than 0.05. These low values indicated that these tests are statistically significant. These ANOVA results indicated that these 6 linear types are acceptable to be applied in the adsorption of MB by using NRH.

Table 2: ANOVA

Type1					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	6.3747	6.3747	286.9417	1.496E-07
Residual	8	0.1777	0.0222		

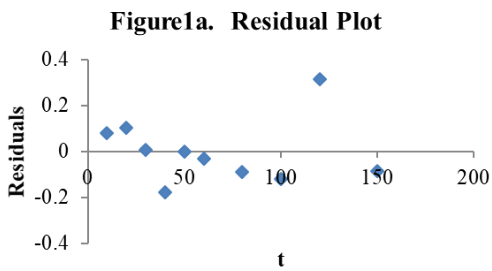
Total	9	6.5524			
Type 2					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	7200.535	7200.535	597.8557	8.357E-09
Residual	8	96.3515	12.0439		
Total	9	7296.8864			
Type 3					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.0070	0.0070	164.4642	1.29E-06
Residual	8	0.0003	4.235E-05		
Total	9	0.0073			
Type 4					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1.3705	1.3705	164.4642	1.29E-06
Residual	8	0.0667	0.0083		
Total	9	1.4372			
Type 5					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.6410	0.6410	50.0737	0.0001
Residual	8	0.1024	0.0128		
Total	9	0.7434			
Type 6					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.0012	0.0012	50.0737	0.0001
Residual	8	0.0002	2.436E-05		
Total	9	0.0014			

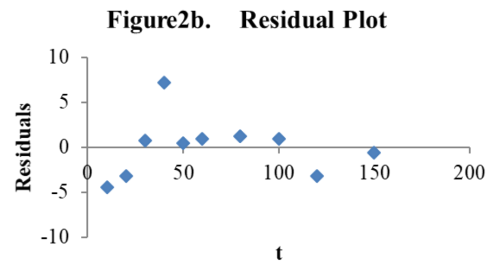
Table 3: ANOVA

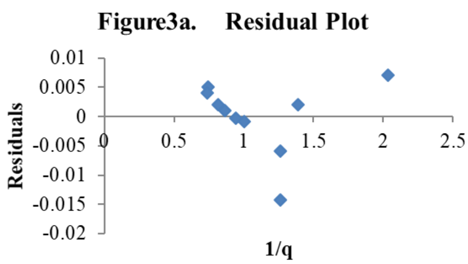
Type1								
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	0.5931	0.0857795	6.9139151	0.0001228	0.3952642	0.7908798	0.3952642	0.7908798
X Variable 1(t)	0.0183945	0.0010859	16.939354	1.496E-07	0.0158904	0.0208986	0.0158904	0.0208986
Type 2								
Intercept	18.645711	1.9972666	9.3356146	1.415E-05	14.040006	23.251416	14.040006	23.251416
X Variable 1 (1/t)	0.6182184	0.0252839	24.451089	8.357E-09	0.5599137	0.6765231	0.5599137	0.6765231
Type 3								

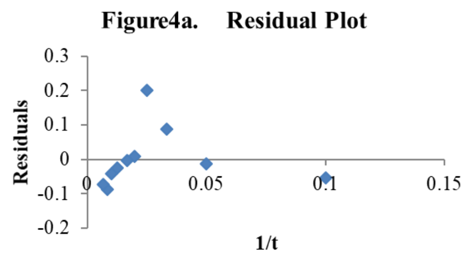
Intercept	-0.048772	0.0063487	-7.68224	5.839E-05	-0.063412	-0.034132	-0.063412	-0.034132
X Variable 1 (q/t)	0.0696138	0.0054282	12.824361	1.29E-06	0.0570963	0.0821314	0.0570963	0.0821314
Type 4								
Intercept	0.7194346	0.04176	17.227857	1.312E-07	0.623136	0.8157332	0.623136	0.8157332
X Variable 1 (q)	13.698622	1.0681719	12.824361	1.29E-06	11.235413	16.161831	11.235413	16.161831
Type 5								
Intercept	1.4520011	0.0741231	19.589045	4.796E-08	1.2810729	1.6229294	1.2810729	1.6229294
X Variable 1 (1/q)	-21.28822	3.0083928	-7.076276	0.0001044	-28.22558	-14.35085	-28.22558	-14.35085
Type6								
Intercept	0.0617834	0.0058921	10.485779	5.95E-06	0.0481962	0.0753707	0.0481962	0.0753707
X Variable 1 (t)	-0.040503	0.0057238	-7.076276	0.0001044	-0.053702	-0.027304	-0.053702	-0.027304

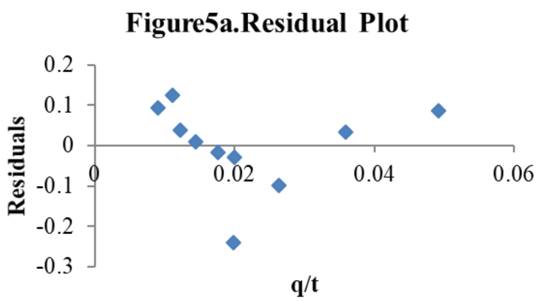
Residual Plot, Line Fit Plot, and Normal Probability Plot can be obtained from the Analysis Toolpak in EXCEL. The residual plot can be used to estimate whether the observed or predicted error (residual residuals) is consistent with the random error (stochastic error). Figure 1a-6a were the Residual Plots of these 6 linear types. These scatter plots display a fairly random pattern in the fig 1a to fig 6a. This random pattern proposes that the transformation of 6 linear types to achieve linearity were successful. Also, the residual distribution pattern of the linear type 2 were better than the other 5 linear types, it indicated that the type 2 was the best transformation among these linear types .











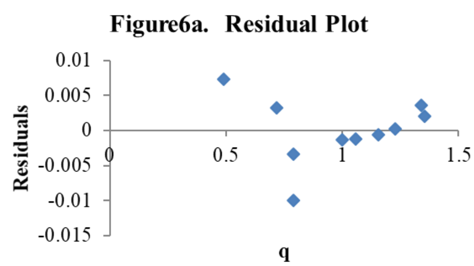
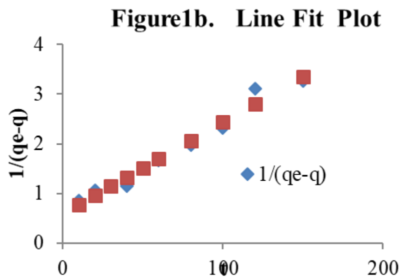
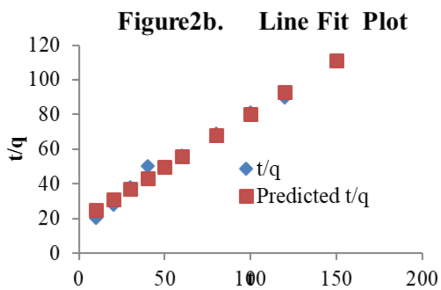
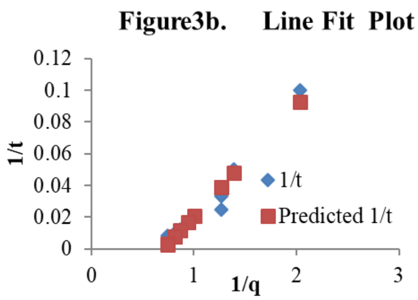
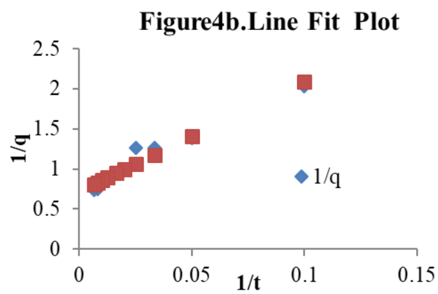


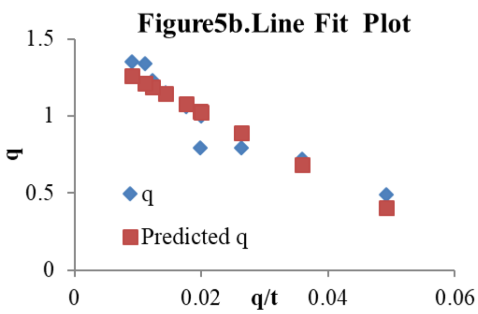
Figure 1b-6b were the Line Fit Plots of these 6 linear types. From Figure 1b to Figure 6b, it can be found that the predicted values calculated by the six linear equations are roughly the same as the experimental values. At the same time, from Figure 1b to Figure 6b, it can be found that Figure 2b shows that the result of the type 2 linear equation is more accurate than the results of other linear equations.

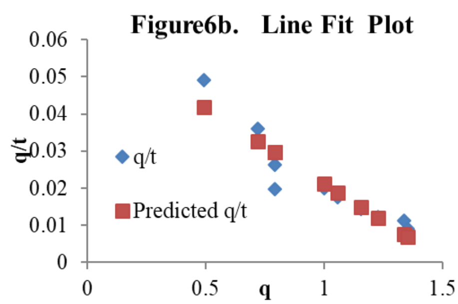












IV. Conclusion

The original pseudo-second-order equation is a nonlinear equation. However, the application of nonlinear equations to calculate or simulate experimental data often increases the difficulty of use. In this study, 6 different linear equations are derived from the original nonlinear type of pseudo-second-order equation. Therefore, many researchers have applied different processes to convert this nonlinear second-order equation into a linear equation. There are currently 6 types of second-order equation linear equations searched in the literature. In this study, these 6 different linear equations are used to analyze the experimental data. There are currently many kinds of mathematical software that can be used to perform calculations and simulations of these 6 equations applied to experimental data. But most of these mathematical software require additional purchases. At present, only EXCEL will appear in Microsoft's windows system for free along with the purchase of computers. In this study, analysis toolpak contained in EXCEL will be used to analyze the accuracy of the 6 linear equations applied to the adsorption of MB by NRH. The Regression Statistics data and ANOVA data obtained by analysis toolpak of excel show that these 6 linear equations can get good prediction values. Among them, the second type of linear equation can get the most accurate prediction value. Similarly, the residual plot and line fit plot obtained by the analysis toolpak of excel show that these six linear equations can get good prediction values. Among them, the second type of linear equation can get the most accurate prediction value. In this study, compared with the difficulty of using nonlinearity, the six different forms of linear equations after linearization can use the easier-to-operate and free EXCEL to calculate the predicted value similar to the experimental data.

References

[1] El-Khaiary, M. I., G. F. Malash and Y.-S. Ho (2010). "On the use of linearized pseudo-second-order kinetic equations for modeling adsorption systems." Desalination 257(1): 93-101.

[2] Ho, Y. and G. McKay (1998). "A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents." Process Safety and Environmental Protection 76(4): 332-340.

[3] Huang, Y.-T., L.-C. Lee and M.-C. Shih (2018). "A Study on the pseudo-second-order kinetic equation for the adsorption of methylene blue onto nitric acid-treated rice husk: Comparison of linear methods." source: International Journal of Scientific and Research Publications (IJSRP) 8(6).

[4] Huang, Y.-T. and M.-C. Shih (2020). "Application of Excel Spreadsheet for comparative analysis of linearized expressions of kinetics modelling for the adsorption of methylene blue on rice husk."

[5] Huang, Y.-T. and M.-C. Shih (2020). "Application of Excel Spreadsheet for comparative analysis of linearized expressions of kinetics modelling for the adsorption of methylene blue on rice husk." International Journal of Scientific and Research Publications 10(6): 548-554.

[6] Xiao, W., X. Jiang, X. Liu, W. Zhou, Z. N. Garba, I. Lawan, L. Wang and Z. Yuan (2020). "Adsorption of organic dyes from wastewater by metal-doped porous carbon materials." Journal of Cleaner Production: 124773.

ACKNOWLEDGEMENT

The authors acknowledge the effort of all students and graduates of Bioprocess Engineering and Fermentation Lab in

Department of Biological Science and Technology, I-Shou University for their experiment operation.

AUTHORS

First Author –Yu-Ting Huang, assistant professor, Department of Nutrition, I-Shou University. No.8, Yida Rd., Jiaosu Village, Yanchao District, Kaohsiung City 82445, Taiwan, R.O.C., email address: ythuang@isu.edu.tw.

Second Author–Ming-Cheng Shih, assistant professor, Department of Biological Science & Technology, I-Shou University. No.8, Yida Rd., Jiaosu Village, Yanchao District, Kaohsiung City 82445, Taiwan, R.O.C., email address: mchshih@isu.edu.tw.

Correspondence Author –Ming-Cheng Shih, email address: mchshih@isu.edu.tw, alternate email address: mchshih@gmail.com, Tel: +886-7-6151100 ext.7321, Fax: +886-7-6577056, Present address: Department of Biological Science & Technology, I-Shou University. No.8, Yida Rd., Jiaosu Village, Yanchao District, Kaohsiung City 82445, Taiwan, R.O.C.