Application of Statistical Data Analysis in Comparative Study of Different Linearized Expressions of Pseudo-Second-order Kinetics of Methylene Blue Adsorption on Hydrochloric Acid-Treated Rice Husk

Yu-Ting Huang[1], Ming-Cheng Shih2[*]

[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.12.06.2022.p12642
http://dx.doi.org/10.29322/IJSRP.12.06.2022.p12642

Paper Received Date: 2nd June 2022
Paper Acceptance Date: 16th June 2022
Paper Publication Date: 20th June 2022

Abstract- Artificial dyes had been used for over a century, and there are numerous varieties of synthetic dyes used in many different industries, which includes fabric industry, pharmaceutical industry, and so on. However, synthetic dyes are not easily degraded by bacteria and a few dyes are hazardous. As a result of the widespread usage of artificial colors, wastewater released from the facility will cause water contamination if not handled. The adsorption approach is presently an inexpensive and greater typically used approach. In order to get higher adsorption efficiency, researchers studied the adsorption mechanism using different exceptional kinetic equations. This study's results are compatible with nonlinear pseudo-second-order kinetic equations. Nonlinear equations, on the other hand, make calculation and simulation more challenging. As a result, many academics use the linearization technique to turn this nonlinear equation into six exceptional linear equations. The Analysis ToolPak in EXCEL was utilized in this work to examine the six various types of linear equations used to determine the estimated value of sorption of methylene blue onto hydrochloric acid-treated rice husk. According to the analytical results, these linear equations may be used to produce reliable prediction values. The second form of linear equation, on the other hand, can provide more accurate prediction values than the other five equations.

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

I. Introduction

Humans have long used natural dyes, such as plant dyes or mineral dyes, to dye clothing. However, due to the confined production of natural dyes and the instability of dyeing, dye production is not large. This quandary used to be not accelerated until the first artificial dye used to be developed. More than a thousand different artificial dyes were then synthesized. These synthetic dyes are now not solely cheap, in addition to being used for dyeing clothes, however also used in medicine, food, etc. Artificial dyes also have major disadvantages. They are now not effortlessly decomposed through microorganisms like natural dyes, and they are additionally extra toxic than natural dyes. Therefore, when artificial colorants are widely used in various industries, these industries will produce a massive amount of colored wastewater. If these colored effluents are directly discharged into natural water without treatment, the environment will be heavily polluted (Xiao, Jiang et al. 2020). Therefore, eradication of dye contaminants in handling wastewater has been considered. The most frequently applied procedures for eradication of dye are biological, physical or even chemical methods (Shih 2012). Each one of these techniques has various dye removal abilities, principal expenses, and operating rates. Adsorption refers to the passive and physico-chemical binding of the dye to the surface of the adsorbent, is now extensively identified as a powerful and economically possible process for the removal of dye pollution from wastewaters (Chowdhury and Das Saha 2011). The research on adsorption is important for getting rid of dye pollutants. The adsorption kinetics model sheds light on the rate of adsorption of the adsorbent that can be used to predict the adsorption mechanism. Therefore, a comprehensive study of adsorption kinetics models is important. Numerous adsorption kinetics models have been developed to explain the reaction order of adsorption systems based on solution concentration (Chowdhury and Das Saha 2011). The pseudo-second-order kinetic model is the most accepted model in most studies of adsorption kinetic research and is widely applied to explain the evolution of adsorption over time under non-equilibrium conditions. (Ho, Ng et al. 2000). The pseudo-second-order model can be done using altered equations that have been established over the past few decades. Among these equations, Ho's equation has been widely used in the course of the previous decade to test the correlation of adsorption data to pseudo-second-order kinetic models because it is simple and suitable for many adsorption systems. (Shahwan 2014). Since the type of pseudo-second-order introduced in the literature is nonlinear, a nonlinear regression method was used to assess the values of q_e and K_2 expects to match the equation to the experimental data (El-Khaiary, Malash et al. 2010). The calculation of pseudo-second-order equations through the use of the non-linear regression technique provides an extra hard calculated method for figuring out equation parameters and the scientists want to apply a few unique software to solve the non-linear regression equation. For these reasons, researchers try to utilize a simple way to approach the pseudo-second-order equation. A normally efficient approach is to apply linearized forms of pseudo-second-order equations to supplant the non-straight type of pseudo-second-order equations to compute 2 parameters, q_e and K_2. This linear regression approach is usually used to anticipate the pseudo-second-order parameters because it requires only little comprehension of the data fitting process, and is without problems solved through the usage of Excel or comparable spreadsheet software (El-Khaiary, Malash et al. 2010, Huang and Shih 2020). However, relying at the approach of the pseudo-second-order equation linearized, the blunder distribution might move more regrettable. Thus, it becomes an inadequate alternative tactic to apply the linearization technique to evaluate the pseudo-second-order parameters.

With this study, the statistical data are calculated by applying the linear expressions of six types of pseudo-second-order kinetic equations through the usage of the analysis toolpak in EXCEL, and the optimal linear expression is found based on the statistical data and comparison figures.

II. Materials and Methods

The particular experimental data applied on this study was acquired from the literature (Shih 2012). The adsorbent applied withinside the literature was rice husk treated with hydrochloric acid (HRH) and the dye applied withinside the literature was methylene blue (MB). The quantity of dye adsorbed at time t (qt) and the quantity of dye adsorbed at equilibrium period (q_e), is computed via way of means of the subsequent equations (Djeribi and Hamdaoui 2008, Huang and Shih 2021):

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

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

Where V is the volume (L) of the dye solution. Ci, Ct and Ce (mg/L) are the dye concentrations in the liquid phase at the initial time t, and at the time of equilibrium, respectively. M is the mass of adsorbent used (g).

The differential form of the pseudo-second order equation derived primarily based on the solid phase adsorption capacity can be composed as follows (Ho and McKay 1999):

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

where q_t (mg/g) is that the quantity of MB combined on the surface of HRH at time t (min); q_e is that the quantity of MB combined at equilibrium (mg/g) and K_2, the adsorption rate constant (min^{-1}). The integral of equation [3] for the boundary conditions from t = 0 to t = t and from q_t = 0 to q_t = q_t is (Ho and McKay 1999, Huang and Shih 2021):

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

Which is that the linearized sorts of the integrated rate law for the pseudo-second-order equation. Eq.[4] are the primary kind of linearized sorts of pseudo-second-order equation. Eq.[4] would be rearranged to reap some other five various linearized sorts of pseudo-second-order expressions (Kumar 2006, Hamdaoui, Saoudi et al. 2008, Chowdhury and Das Saha 2011, Huang and Shih 2021):

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

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

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

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

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

III. Results and Discussion

In this study, the experimental results of HRH adsorption of MB (Shih 2012) used the Analysis Toolpak in Excel to investigate the statistical data through making use of the experimental results to six one-of-a-kind linear equations. Table 1 is an analysis of the regression statistics table, which shows that some of the multiple R values obtained from the six linear types of pseudo-second-order equations differ. Type 2's multiple R-value is closer to 1 than the multiple R-values of five other linear types. Type 2's R^2 value is closer to 1 than the R^2 values of five other linear types. The highest multiple R value and the highest R^2 values of the types 2 is the most excellent linear form of the pseudo-second-order equation.

Table1: Regression Statistics

	type1	*type 2*	*type 3*	*type 4*	*type 5*	*Type6*
Multiple R	0.9893	0.9952	0.9873	0.9873	0.9531	0.9531
R Square	0.9788	0.9905	0.9748	0.9748	0.9084	0.9084
Adjusted R Square	0.9761	0.9893	0.9716	0.9716	0.8970	0.8970
Standard Error	0.1860	3.1083	0.0048	0.0849	0.0904	0.0033
Observations	10	10	10	10	10	10

The values of variance (ANOVA) have been given in Tables 2 and 3. The significance F values of the six different linear expressions in Table 2 are all under 0.05, indicating that the overall regression equation is significantly effective. The P-value refers to the significance test degree of the coefficient. Generally, it is not statistically significant if it is greater than 0.05, and it is statistically significant if it is less than 0.05. The P values of the 6 linear equations in Table 3 are all less than 0.05. These low values suggest that these tests are statistically significant. These ANOVA results indicate that these 6 linear categories are acceptable for application in MB adsorption by HRH.

Table 2: ANOVA

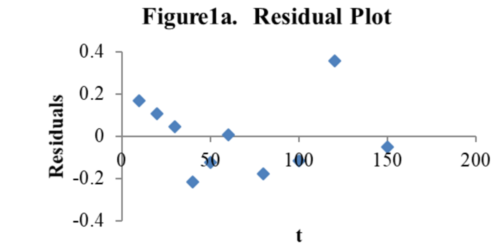
Type1					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	12.755994	12.755994	368.85181	5.601E-08
Residual	8	0.2766638	0.034583		
Total	9	13.032658			
Type 2					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	8048.5275	8048.5275	833.07041	2.247E-09
Residual	8	77.29025	9.6612813		
Total	9	8125.8178			
Type 3					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.0071193	0.0071193	309.36056	1.115E-07
Residual	8	0.0001841	2.301E-05		
Total	9	0.0073034			
Type 4					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	2.229564	2.229564	309.36056	1.115E-07
Residual	8	0.0576561	0.007207		
Total	9	2.2872201			
Type 5					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.6478776	0.6478776	79.365527	1.997E-05
Residual	8	0.0653057	0.0081632		
Total	9	0.7131832			
Type 6					
	df	*SS*	*MS*	*F*	*Significance F*

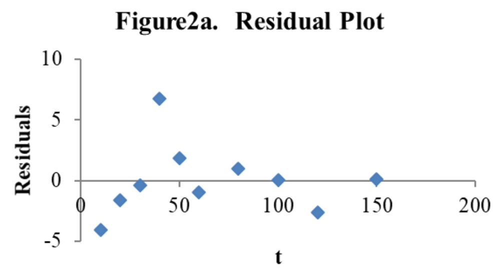
Regression	1	0.0008472	0.0008472	79.365527	1.997E-05
Residual	8	8.54E-05	1.068E-05		
Total	9	0.0009326			

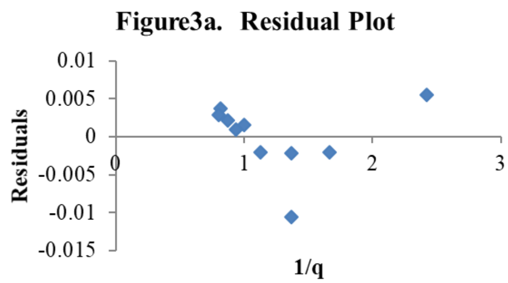
Table 3: ANOVA

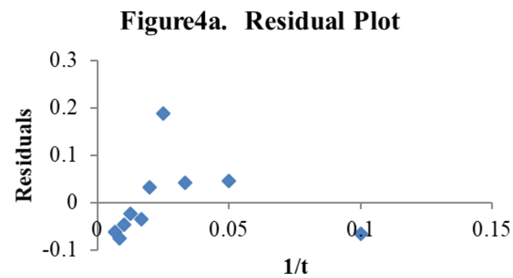
Type1								
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	0.5098378	0.1070245	4.76375	0.00142	0.2630389	0.7566366	0.2630389	0.7566366
X Variable 1(t)	0.0260206	0.0013548	19.205515	5.601E-08	0.0228963	0.0291449	0.0228963	0.0291449
Type 2								
Intercept	21.811163	1.7888306	12.192973	1.898E-06	17.686112	25.936214	17.686112	25.936214
X Variable 1 (1/t)	0.6536086	0.0226452	28.862959	2.247E-09	0.6013886	0.7058286	0.6013886	0.7058286
Type 3								
Intercept	-0.040789	0.0042082	-9.692886	1.071E-05	-0.050493	-0.031085	-0.050493	-0.031085
X Variable 1 (q/t)	0.0557911	0.003172	17.588649	1.115E-07	0.0484764	0.0631057	0.0484764	0.0631057
Type 4								
Intercept	0.7438704	0.0388359	19.154177	5.72E-08	0.6543146	0.8334262	0.6543146	0.8334262
X Variable 1 (q)	17.47219	0.9933788	17.588649	1.115E-07	15.181455	19.762926	15.181455	19.762926
Type 5								
Intercept	1.4107869	0.0635115	22.213076	1.783E-08	1.264329	1.5572448	1.264329	1.5572448
X Variable 1 (1/q)	-26.35658	2.9585109	-8.908733	1.997E-05	-33.17892	-19.53425	-33.17892	-19.53425
Type6								
Intercept	0.0503811	0.0036523	13.794219	7.366E-07	0.0419588	0.0588034	0.0419588	0.0588034
X Variable 1 (t)	-0.034467	0.0038689	-8.908733	1.997E-05	-0.043389	-0.025545	-0.043389	-0.025545

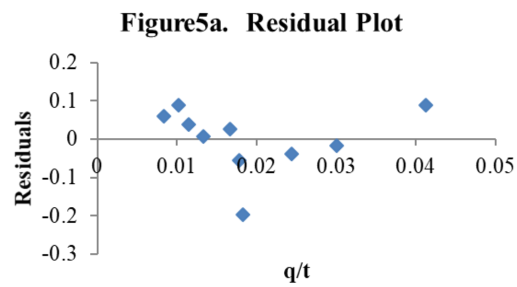
The Residual Plots, and Line-fit Plots are available from EXCEL's Analysis Toolpack. Residual plots can be used to estimate whether the observed or predicted error (residual) matches the random error (stochastic error). Figure 1a-6a shows the residual plots of these six linear types. These scatter plots show a fairly random pattern in Figures 1a through 6a. This random pattern shows that the six linear types have been successfully transformed to achieve linearity. Furthermore, the residual distribution model of linear type 2 is b superior to the other five linear types, which indicates that type 2 is the best transformation of these linear types.

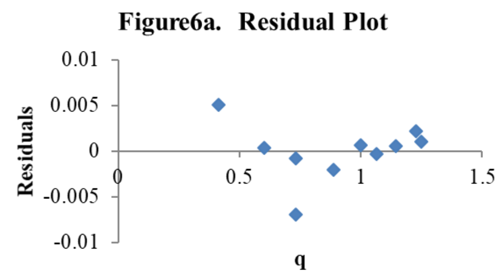




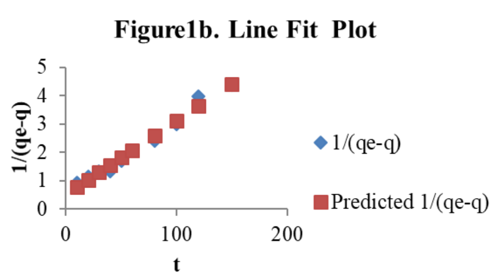


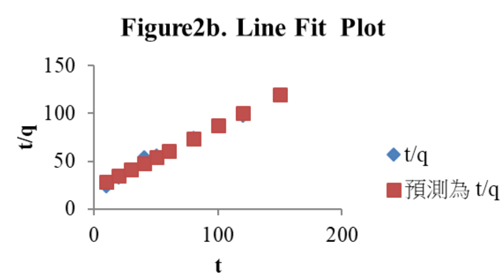


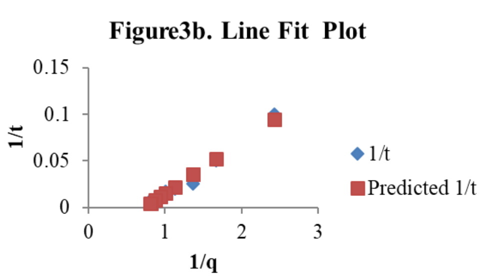


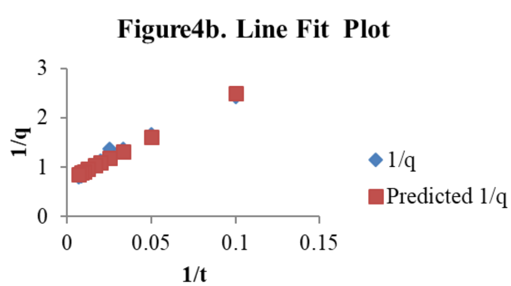


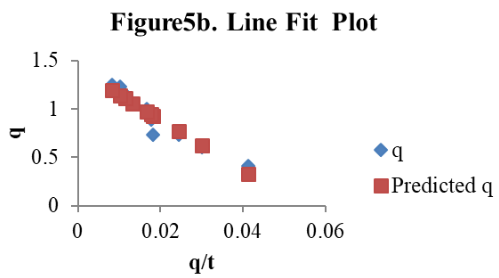
Linear fit plots of these six linear types have been shown in Figure 1b to Figure 6b. From Figure 1b to Figure 6b, the predicted values calculated by the six linear equations are almost the same as the experimental values. At the same time, Figure 2b shows that the results of linear equations of type 2 are more accurate than the results of other linear equations from Figure 1b to Figure 6b.

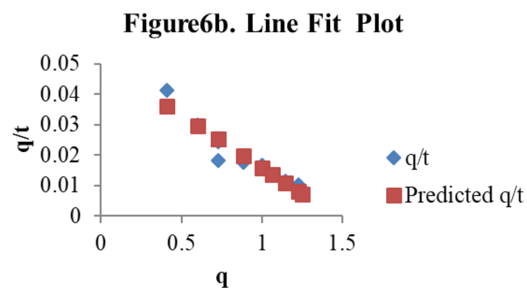












IV. Conclusion

The authentic pseudo-second-order equation is a nonlinear equation. However, the utility of nonlinear equations to calculate or simulate experimental results frequently will increase the problem of use. In this study, 6 one of a kind linear equation are derived from the authentic nonlinear pseudo-second-order equation. As a result, many researchers have carried out one of a kind tactics to transform this nonlinear second-order equation right into a linear equation. There are presently 6 sorts of second-order equation linear equations searched in the literature. In this study, these 6 one of a kind linear equation are used to analyze the experimental data. There are presently many types of mathematical software program available for performing calculations and simulations of these six equations when applied to experimental data. However, the majority of these mathematical software packages require additional purchases. At present, solely EXCEL will show up in Microsoft`s home windows device for free alongside with the buy of Microsoft's low-cost office software at the same time as the purchase of a computer. In this study, analysis toolpak contained in EXCEL will be used to analyze the accuracy of the 6 linear equations utilized to the adsorption of MB by way of HRH. The Regression Statistics facts and ANOVA information received with the aid of analysis toolpak of excel exhibit that these 6 linear equations can get appropriate prediction values. Among them, the 2d kind of linear equation can get the most correct prediction value. Similarly, the residual plot and line fit plot acquired by way of the analysis toolpak of excel exhibit that these six linear equations can get appropriate prediction values. Among them, the 2d kind of linear equation can get the most correct prediction value. In this study, in contrast with the use of nonlinearity, the six one-of-a-kind types of linear equations after linearization can use the easier-to-use EXCEL to perform calculations and compare the experimental data to obtain fairly accurate calculation estimates.

ACKNOWLEDGEMENT

The authors acknowledge the effort of all graduate and non-graduate students of Bioprocess Engineering and Fermentation Lab in Department of Biological Science and Technology, I-Shou University for their experiment operation.

References

[1] Chowdhury, S. and P. Das Saha (2011). "Comparative analysis of linear and nonlinear methods of estimating the pseudo-se``cond-order kinetic parameters for sorption of Malachite green onto pretreated rice husk." Bioremediation Journal 15(4): 181-188.

[2] Djeribi, R. and O. Hamdaoui (2008). "Sorption of copper (II) from aqueous solutions by cedar sawdust and crushed brick." Desalination 225(1-3): 95-112.

[3] 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.

[4] Hamdaoui, O., F. Saoudi, M. Chiha and E. Naffrechoux (2008). "Sorption of malachite green by a novel sorbent, dead leaves of plane tree: Equilibrium and kinetic modeling." Chemical Engineering Journal 143: 73-84.

[5] Ho, Y., J. Ng and G. McKay (2000). "Kinetics of pollutant sorption by biosorbents: review." Separation & Purification Reviews 29(2): 189-232.

[6] Ho, Y. S. and G. McKay (1999). "Pseudo-second order model for sorption processes." Process Biochemistry 34(5): 451-465.

[7] 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."

[8] Huang, Y.-T. and M.-C. Shih (2021). "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." International Journal of Scientific and Research Publications 11(6): 692-698.

[9] Kumar, K. V. (2006). "Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon." Journal of hazardous materials 137(3): 1538-1544.

[10] Shahwan, T. (2014). "Sorption kinetics: Obtaining a pseudo-second order rate equation based on a mass balance approach." Journal of Environmental Chemical Engineering 2(2): 1001-1006.

[11] Shih, M.-C. (2012). "Kinetics of the batch adsorption of methylene blue from aqueous solutions onto rice husk: effect of acid-modified process and dye concentration." Desalination and Water Treatment 37(1-3): 200-214.

[12] 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.

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.