Comparative Analysis of Linearized Expressions for Pseudo-Second-Order Kinetics Modeling of Methylene Blue Adsorption on Sulfuric Acid-Treated Rice Husk: A Statistical Data Analysis Approach

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Abstract- Artificial dyes have been employed for over a century in a wide variety of industries, including the textiles and pharmaceutical sectors. However, synthetic dyes are often poorly biodegradable and can be hazardous to human health and the environment. When wastewater containing synthetic dyes is discharged from these facilities without treatment, it can lead to water contamination. Adsorption is a cost-effective and widely adopted method for removing synthetic dyes from wastewater. To improve the efficiency of adsorption, researchers have investigated the adsorption mechanism using different kinetic equations. The findings of this study are consistent with the nonlinear pseudo-second-order kinetic equations present challenges in calculations and simulations. To overcome these challenges, scientists often use the linearization technique to transform the nonlinear equations into six linear equations. In this study, the Analysis ToolPak in Excel was used to evaluate the six different types of linear equations for estimating the sorption value of methylene blue onto sulfuric acid-treated rice husk. The results of the analysis show that these linear equations can provide reliable prediction values. Specifically, the third and fourth forms of linear equations offer more accurate predictions compared to the others.

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

I. INTRODUCTION

For centuries, humans have relied on natural dyes derived from plants and minerals to add color to textiles. However, the widespread production of these dyes has been hampered by their limited availability and the challenges they pose during the dyeing process. This issue was not addressed until the development of the first synthetic dye, which resulted in the synthesis of over a thousand different artificial dyes. These synthetic dyes are not only cost-effective for dyeing textiles, but they also find applications in medicine, food, and various other fields. On the other hand, the utilization of synthetic dyes has significant disadvantages. Unlike natural dyes, artificial colorants are not easily broken down by microorganisms and are more harmful. Consequently, their widespread application in various industries can result in the production of a considerable amount of colored wastewater. If this effluent is released into natural water sources without proper treatment, it can cause significant environmental contamination. (Xiao, Jiang et al. 2020). Consequently, the removal of dye contaminants from wastewater has become a critical concern. The most commonly used methods for removing dyes are biological, physical, or chemical processes (Shih 2012). Each of the techniques used for removing dyes has varying dye removal efficiencies, costs, and operational rates. Indeed, adsorption is a widely recognized and economically feasible approach for the removal of dye pollutants from wastewater. This process entails the passive and physicochemical binding of dyes to the surface of an adsorbent material (Chowdhury and Das Saha 2011). Research on adsorption is crucial for mitigating dye contamination. The study of adsorption kinetics models is crucial as they offer valuable insights into the rate of adsorption and can be utilized to predict the underlying adsorption mechanism. Therefore, a comprehensive examination of these models is essential. Several adsorption kinetics models have been developed to describe the reaction order of adsorption systems, taking into consideration the concentration of the solution(Chowdhury and Das Saha 2011). The pseudo-second-order kinetic model is widely recognized as the most suitable model for investigating adsorption kinetics. It has been extensively employed in research to comprehend the temporal evolution of adsorption under non-equilibrium conditions. This model has gained substantial acceptance and is considered the most appropriate approach for analyzing adsorption kinetics (Ho, Ng et al. 2000). Over the past few decades, various equations have been developed to describe the pseudo-second-order kinetic model. Among these equations, Ho's equation has gained significant popularity in the last decade for testing the correlation of adsorption data with the pseudo-second-order kinetic model. This equation is widely used due to its simplicity and applicability to a wide range of adsorption systems (Shahwan 2014). As the pseudo-second-order model described in the literature is nonlinear, the estimation of q_e (equilibrium adsorption capacity) and K_2 (rate constant) involves the application of a nonlinear regression method. This method entails fitting the experimental data to the equation, enabling the determination of the most accurate values for q_e and K_2 by minimizing the discrepancies between the observed data and the model predictions. (El-Khaiary, Malash et al. 2010). Researchers seek simpler methods to solve the pseudo-second-order parameters in nonlinear regression for equations. They often turn to linearized versions of the pseudo-second-order equations as a more straightforward approach to estimate the parameters q_e and K_2. This linear regression method is commonly used for predicting the pseudo-second-order parameters because it only requires basic knowledge of data fitting and can be easily solved using Excel or similar spreadsheet software(El-Khaiary, Malash et al. 2010, Huang and Shih 2020). Nonetheless, the degradation of the error distribution can occur depending on the specific approach employed for linearizing the pseudo-second-order equation. As a consequence, utilizing the linearization technique for the evaluation of pseudo-second-order parameters is deemed inappropriate as an alternative methodology.

In this research, the statistical data were computed utilizing the EXCEL analysis toolpak, employing linear formulations of six unique variations of pseudo-second-order kinetic equations. The determination of the optimal linear formulation was achieved through a thorough analysis of the statistical data and comparative figures.

II. MATERIALS AND METHODS

The experimental data utilized in this study were sourced from the published literature (Shih 2012). The adsorbent employed in the literature was rice husk treated with sulfuric acid (SRH), while the dye employed was methylene blue (MB). The adsorption quantities of dye at a given time (q_t) and at equilibrium (q_e) were determined through the utilization of the subsequent equations. (Djeribi and Hamdaoui 2008, Huang and Shih 2021):

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

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

The equations provided to calculate the amount of dye adsorbed involve the consideration of specific variables. These variables include the volume (V in liters) of the dye solution, the initial dye concentration (C_i in milligrams per liter), the dye concentration at a given time (C_t in milligrams per liter), the dye concentration at equilibrium (C_e in milligrams per liter), and the mass of the adsorbent used (M in grams).

Within the existing body of literature, the derivation of the pseudo-second-order equation in its differential form primarily stems from the examination of the adsorption capacity pertaining to the solid phase. This formulation can be expressed as follows (Ho and McKay 1999):

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

In the specific context of this research study, the variable q_t (measured in milligrams per gram) signifies the quantity of methylene blue (MB) that has been adsorbed onto the surface of sulfuric acid-treated rice husk (SRH) at a given time t (measured in minutes). Conversely, q_e represents the amount of MB that has reached equilibrium adsorption (measured in milligrams per gram), while K_2 denotes the adsorption rate constant (expressed in inverse minutes). In order to calculate the definite integral of equation [3] within the prescribed boundary conditions, which span from t = 0 to t = t and from $q_t = 0$ to $q_t = q_t$, the subsequent expression is utilized (Ho and McKay 1999, Huang and Shih 2021):

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

The linearized representations of the integrated rate law corresponding to the pseudo-second-order equation, Equation [4], constitute the initial category of linearized forms for pseudo-second-order equations. To establish a supplementary set of five distinct linearized forms for pseudo-second-order expressions, Equation [4] can be rearranged employing the methodologies put forth by the proposed approaches (Kumar 2006, Hamdaoui, Saoudi et al. 2008, Chowdhury and Das Saha 2011, Huang and Shih 2021):

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

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

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

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

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

III. RESULTS AND DISCUSSION

The experimental data concerning the adsorption of methylene blue (MB) by sulfuric acid-treated rice husk (SRH), as obtained from Shih's published work (Shih 2012) , underwent statistical analysis. The Analysis Toolpak in Excel was employed for this purpose. Six different linear equations were utilized to fit the data, and the resulting regression statistics were presented in Table 1. Among the six types of pseudo-second-order linear equations employed in this study, the multiple R-values exhibited variation. Notably, Type 3 and Type 4 displayed multiple R-values closer to 1 compared to the other four linear types. Similarly, the R^2 values of Type 3 and Type 4 were closer to 1 than those of the other four linear types. Consequently, Type 3 and Type 4 demonstrated the highest multiple R-values and the highest R2 values among all the types, indicating their superiority as linear representations of the pseudo-second-order equation.

Table1: Regression Statistics

	type1	*type 2*	*type 3*	*type 4*	*type 5*	*Type6*
Multiple R	0.9687	0.9725	0.9783	0.9783	0.8816	0.8816
R Square	0.9383	0.9458	0.9570	0.95670	0.7772	0.7772
Adjusted R Square	0.9306	0.9391	0.9516	0.9516	0.7493	0.7493
Standard Error	0.2550	8.3457	0.0063	0.1519	0.1274	0.0038
Observations	10	10	10	10	10	10

The values of variance (ANOVA) have been given in Tables 2 and 3. In the ANOVA table, when the F value associated with the linear expression is found to be statistically significant at a significance level of 0.05, it indicates that the regression equation is deemed significantly effective. Upon examination of Table 2, it is observed that the significance F values for the six different linear expressions presented are all below the threshold of 0.05. This finding unequivocally confirms the significant effectiveness of the overall regression equation.// The P-value, which denotes the degree of significance in coefficient testing, is considered statistically insignificant if it exceeds 0.05, while it is deemed statistically significant if it is below 0.05. Notably, the P values corresponding to the six linear equations outlined in Table 3 are all below 0.05. These notably low values strongly suggest the statistical significance of the conducted tests. The ANOVA results further affirm the suitability of these six linear categories for practical implementation in the adsorption of MB by SRH.

Table 2: ANOVA

Type1					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	7.9113	7.9113	121.6279	4.06853E-06
Residual	8	0.5204	0.0650		
Total	9	8.4316			
Type 2					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	9728.1386	9728.1386	139.6693	2.4082E-06
Residual	8	557.2098	69.6512		
Total	9	10285.3484			
Type 3					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.0070	0.0070	177.9929	9.52456E-07
Residual	8	0.0003	3.92671E-05		
Total	9	0.0073			
Type 4					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	4.1075	4.1075	177.9929	9.52456E-07
Residual	8	0.1846	0.0231		

Total	9	4.2921			
Type 5					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.4531	0.4531	27.9011	0.0007
Residual	8	0.1299	0.0162		
Total	9	0.5830			
Type 6					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.0004	0.0004	27.9011	0.0007
Residual	8	0.0001	1.47929E-05		
Total	9	0.0005			

Table 3: ANOVA

Type1								
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	0.5309	0.1468	3.6167	0.0068	0.1924	0.8693	0.1924	0.8693
X Variable 1(t)	0.0205	0.0019	11.0285	0.0000	0.0162	0.0248	0.0162	0.0248
Type 2								
Intercept	34.1474	4.8030	7.1095	0.0001	23.0716	45.2233	23.0716	45.2233
X Variable 1 (1/t)	0.7186	0.0608	11.8182	2.4082E-06	0.5784	0.8588	0.5784	0.8588
Type 3								
Intercept	-0.0360	0.0052	-6.9120	0.0001	-0.0480	-0.0240	-0.0480	-0.0240
X Variable 1 (q/t)	0.0404	0.0030	13.3414	9.52E-07	0.0334	0.0473	0.0334	0.0473
Type 4								
Intercept	0.921978	0.069493	13.26716	9.94E-07	0.761726	1.08223	0.761726	1.08223
X Variable 1 (q)	23.71511	1.777558	13.3414	9.52E-07	19.61605	27.81416	19.61605	27.81416
Type 5								
Intercept	1.1542	0.0917	12.5800	0.0000	0.9426	1.3657	0.9426	1.3657
X Variable 1 (1/q)	-29.2093	5.5298	-5.2822	0.0007	-41.9610	-16.4575	-41.9610	-16.4575
Type6								
Intercept	0.0340	0.0038	8.9095	2E-05	0.0252	0.0428	0.0252	0.0428
X Variable 1 (t)	-0.0266	0.0050	-5.2822	0.0007	-0.0382	-0.0150	-0.0382	-0.0150

The Residual Plots, and Line-fit Plots are available from EXCEL's Analysis Toolpack. Residual plots serve as a useful tool for assessing the alignment between observed or predicted errors (residuals) and random errors (stochastic errors). They aid in estimating the degree of concordance between these two types of errors. When a residual plot exhibits discernible patterns, such as U-shaped, inverted U-shaped, W-shaped, inverted W-shaped, and similar configurations, it suggests the presence of unaccounted variables or non-linear associations between the variables in the model. Consequently, further refinement or enhancement of the model becomes necessary. Conversely, if the residual plot demonstrates a random distribution pattern, it indicates that the model adheres to the assumptions of linear regression. The residual plots of these six distinct linear types are shown in Figure 1a-6a. The scatter plots in Figures 1a through 6a exhibit a reasonably random arrangement. This indicates that the six linear types have undergone successful transformations to attain linearity

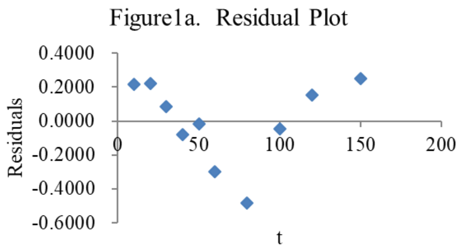
Figure1a. Residual Plot

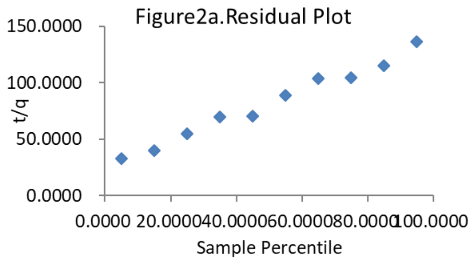
Figure2a.Residual Plot

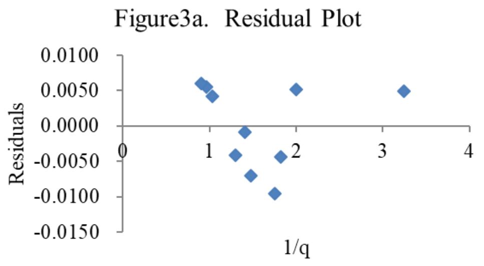
Figure3a. Residual Plot

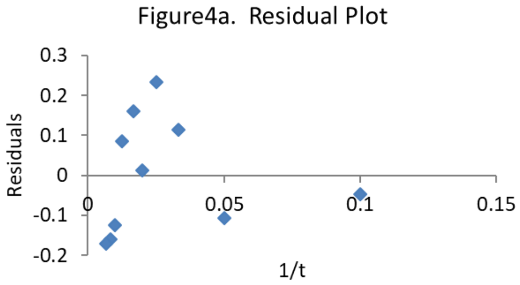
Figure4a. Residual Plot

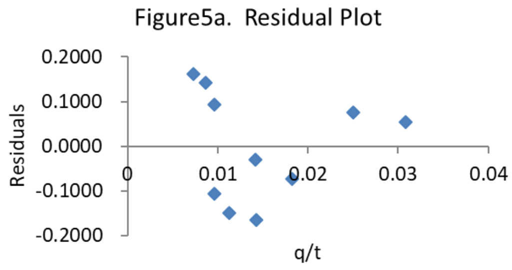
Figure5a. Residual Plot

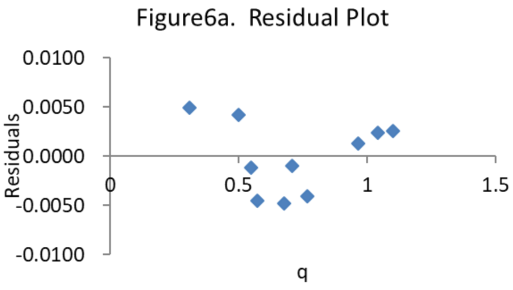
Figure6a. Residual Plot

Line Fit plots depicting the six different linear models are displayed in Figures 1b through 6b. Based on Figures 1b to 6b, it can be observed that there is a significant deviation between the simulated and experimental values in Figures 5b and 6b. Figures 1b and 2b only exhibit minor differences between a few simulated and experimental values. The best agreement between simulated and experimental values is found in Figures 3b and 4b.

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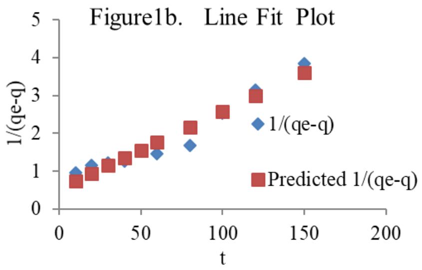

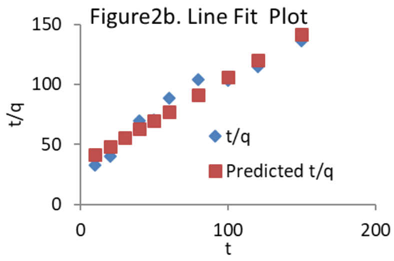

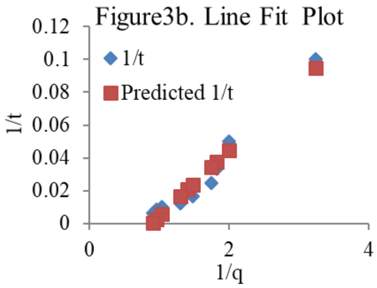

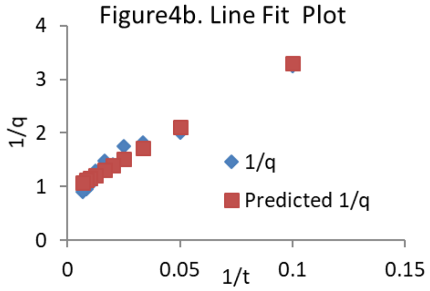

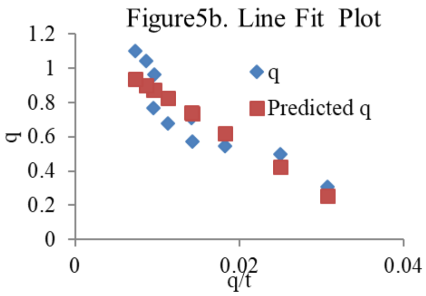

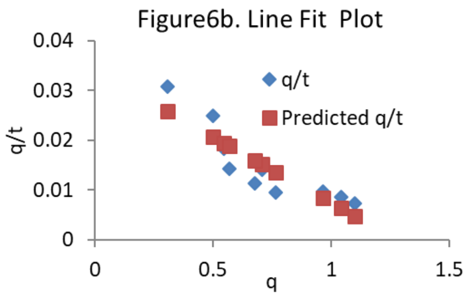

IV. CONCLUSION

The genuine pseudo-second-order equation is inherently nonlinear. However, utilizing nonlinear equations for calculating or simulating experimental results often presents challenges. In this study, six different linear equations were obtained by linearizing the initial nonlinear pseudo-second-order equation. Consequently, researchers have utilized diverse methodologies to linearize this nonlinearity inherent in the second-order equation. Currently, there are six types of linear equations for the second-order equation documented in the literatures. In this research endeavor, the experimental data was analyzed employing the aforementioned set of six unique linear equations. Currently, there exists a wide range of mathematical software programs capable of executing calculations and simulations that incorporate these six equations in tandem with experimental data. However, the majority of these software packages require additional purchases. Presently, only EXCEL, which is included with Microsoft's affordable office software and bundled with a computer purchase, is readily accessible on Microsoft's Windows platform at no additional cost. In this investigation, the accuracy of the six linear equations utilized in the analysis of methylene blue (MB) adsorption by sulfuric acid-treated rice husk (SRH) was evaluated using the Analysis ToolPak integrated within the EXCEL software. The Regression functionality of data analysis in Excel's Analysis ToolPak was utilized to analyze the experimental data obtained from six different methods of linear transformation. It was found that the ANOVA data and residual plot obtained demonstrate the applicability of all six linear transformation methods for calculating simulated values. Through the examination of Statistics data and Line Fit plots, it is confirmed that the third and fourth methods of linear transformation yield the most optimal simulated estimation data.

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REFERENCES

[1] Chowdhury, S. and P. Das Saha (2011). "Comparative analysis of linear and nonlinear methods of estimating the pseudo-second-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.

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