Using XLMiner Analysis ToolPak to analyze the effect of Acid -Treated process on rice husk adsorption

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Abstract- Synthetic dyes have been in use for over a century and have been extensively applied across various industries, including leather, textiles, and pharmaceuticals. However, unlike natural dyes, synthetic dyes are less environmentally friendly due to their poor biodegradability, and some can even be harmful to the environment. Consequently, untreated wastewater from industries using synthetic dyes can lead to water pollution. Various methods exist for treating dye wastewater, with adsorption being particularly economical and effective, making it widely adopted. The efficiency of the adsorption process directly impacts the overall cost of wastewater treatment. Consequently, numerous studies have been conducted to enhance adsorption productivity. Analysts have utilized several kinetic models to investigate the adsorption mechanisms of dyes to identify ways to improve adsorption efficiency. The experimental results of this study align with nonlinear kinetic models. However, nonlinear equations are challenging to calculate and simulate. Therefore, many scholars use linearization techniques to convert these nonlinear equations into linear forms to assess the impact of different acid washing processes on the adsorption efficiency of rice husks. In this study, the XLMiner Analysis ToolPak was employed to predict the effect of various acid washing processes on rice husk adsorption efficiency. The analysis confirmed that these linear equations could create solid expectations. Furthermore, the XLMiner Analysis ToolPak gives reliable statistical analysis data.

Index Terms- XLMiner Analysis ToolPak; acid-treated rice husk; Adsorption; Methylene blue; Kinetics

I. Introduction

Natural dyes, including plant-based and mineral dyes, have been used by humans for painting and textile coloring since ancient times. However, natural dyes cannot be produced in large quantities, and their color stability during the dyeing process is relatively poor, making large-scale production and application challenging. This issue was resolved with the development of the first synthetic dyes, which addressed various problems associated with the large-scale application of natural dyes and facilitated the industrialization of dye production. Consequently, thousands of different synthetic dyes have been created and applied in various fields such as traditional textile dyeing, pharmaceuticals, food, and cosmetics. However, compared to natural dyes, synthetic dyes have several significant disadvantages, particularly in terms of environmental friendliness. For example, synthetic dyes are difficult for microorganisms to degrade, and some dyes are highly toxic. As a result, industries that use synthetic dyes and discharge wastewater containing residual synthetic dyes into natural water bodies without proper treatment cause severe environmental damage. (Xiao, Jiang et al. 2020).

With the extensive application of synthetic dyes in various industries, the process of removing these dyes from factory wastewater has become a critical issue. Biological, physical, and chemical removal methods are currently the most common techniques used in the industry for dye removal (Shih 2012).

Each of these methods has different dye removal efficiencies, costs, and operational rates. Among them, adsorption is recognized as a cost-effective and efficient method for removing synthetic dyes and is widely accepted and applied. The adsorption mechanism involves the passive physicochemical binding of the dye to the surface of the adsorbent (Chowdhury and Das Saha 2011). Thus, research into developing highly efficient and low-cost adsorbents is crucial. Adsorption kinetics studies help understand the adsorption rates of adsorbents and can be further used to predict adsorption mechanisms. Therefore, in-depth investigation into adsorption kinetics is an essential area of research. Currently, many researchers have proposed different ways of doing adsorption at present(Chowdhury and Das Saha 2011). Among the diverse models evolved during the last few decades, the pseudo-second-order (PSO) version is the maximum normally used to explain adsorption kinetics. (Ho, Ng et al. 2000), which is developed by Ho (Shahwan 2014). Since the equation introduced by Ho is nonlinear, nonlinear regression methods are required to fit experimental data to the equation and estimate its parameters (El-Khaiary, Malash et al. 2010). However, solving nonlinear equations using nonlinear regression techniques involves complex methods or specialized software. Therefore, researchers often transform the nonlinear equation into a linearized version of the pseudo-second-order model. This transformation allows the use of linear regression methods to predict PSO parameters, as linear regression requires only basic knowledge of the data fitting process and can be easily performed using Excel or similar spreadsheet software (El-Khaiary, Malash et al. 2010, Huang and Shih 2020). Nevertheless, the error distribution resulting from the linearization of the PSO equation may lead to biased predictions. Therefore, statistical calculations and analyses are used to evaluate whether the linearization of PSO parameters introduces significant bias.

In this study, all statistical data were computed using XLMiner ToolPak. By analyzing the statistical data and comparison charts, the accuracy of the experimental results can be confirmed.

2. Materials and methods

The experimental information applied on this examine had been derived from the author's formerly posted work (Shih 2012). The adsorbents used withinside the look at consist of untreated rice husk (CRH), sulfuric acid-handled rice husk (SRH), nitric acid-handled rice husk (NRH), and hydrochloric acid-handled rice husk The dye used in the literature as a representative dye is methylene blue (MB). The amount of dye adsorbed at time t (q_t) and at equilibrium time (q_e) can be calculated the usage of the subsequent equations: (Djeribi and Hamdaoui 2008, Huang and Shih 2021):

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

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

Where V represents the dye solution's volume(L). On the preliminary and time of equilibrium, respectively, the dye concentrations C_i, C_t, and C_e(mg/L) are displayed. The amount of adsorbent used(g) is M.

In this study, the experimental data was evaluated by proposing two types of kinetic models, including the pseudo-first-order kinetic model, and pseudo-second order kinetic model.

Pseudo-First-Order Kinetic Model:

The pseudo-first-order kinetic model is provided by the Etim, Yakubu et al. 2024 as follow:

$$log(q_e - q_t) = log(q_e) - \frac{K_1}{2.303}t \quad (3)$$

where q_e and q_t characterize the quantity of dye that can be absorbed at equilibrium and time, respectively, and k_1 represents the pseudo-first-order adsorption rate constant.

Pseudo-Second-Order Kinetic Model

The pseudo-second-order kinetic model is represented as (Ho and McKay 1999):

$$\left(\frac{t}{q_t}\right) = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}(t) \quad (4)$$

where pseudo-second-order adsorption has the rate constant k_2.

3. Results and discussion

The statistical analysis of the experimental data, which was obtained from Shih's published work, (Shih 2012) , was carried out using the XLMiner Analysis ToolPak. The data was fitted to three different linear kinetic equations and the regression statistics were shown in Tables 1 and 4. The ANOVA values have been presented in Tables 2 ,3, 5, and 6.

Table1: Regression Statistics of pseudo-first-order kinetic model

	CRH	*HRH*	*SRH*	*NRH*
Multiple R	0.918205	0.979174	0.984784	0.971893
R Square	0.843101	0.958782	0.9698	0.944576
Adjusted R Square	0.825668	0.954203	0.966444	0.938418
Standard Error	0.168694	0.055456	0.040185	0.057241
Observations	11	11	11	11

Table 2: ANOVA of pseudo-first-order kinetic model

CRH					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1.376252	1.376252	48.36166	6.65E-05
Residual	9	0.256118	0.028458		
Total	10	1.632369			
HRH					
	df	*SS*	*MS*	*F*	*Significance F*

Regression	1	0.643839	0.643839	209.3537	1.54E-07
Residual	9	0.027678	0.003075		
Total	10	0.671517			
SRH					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.466692	0.466692	289.0098	3.79E-08
Residual	9	0.014533	0.001615		
Total	10	0.481225			
NRH					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.502564	0.502564	153.385	5.88E-07
Residual	9	0.029488	0.003276		
Total	10	0.532052			

Table 3: ANOVA of pseudo-first-order kinetic model

CRH								
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	0.012363	0.084145	0.146925	0.88643	-0.17799	0.202712	-0.17799	0.202712
X Variable 1(t)	-0.00777	0.001117	-6.95425	6.65E-05	-0.0103	-0.00524	-0.0103	-0.00524
HRH								
Intercept	0.068505	0.027662	2.476554	0.03519	0.005931	0.13108	0.005931	0.13108
X Variable 1 (1/t)	-0.00531	0.000367	-14.4691	1.54E-07	-0.00614	-0.00448	-0.00614	-0.00448
SRH								
Intercept	0.074204	0.020044	3.702013	0.004905	0.028861	0.119547	0.028861	0.119547
X Variable 1 (q/t)	-0.00452	0.000266	-17.0003	3.79E-08	-0.00513	-0.00392	-0.00513	-0.00392
NRH								
Intercept	0.106236	0.028552	3.720818	0.004765	0.041647	0.170824	0.041647	0.170824
X Variable 1 (q)	-0.00469	0.000379	-12.3849	5.88E-07	-0.00555	-0.00384	-0.00555	-0.00384

Table4: Regression Statistics of pseudo-second-order kinetic model

	CRH	*HRH*	*SRH*	*NRH*
Multiple R	0.999859	0.995233	0.972535	0.993376
R Square	0.999718	0.990488	0.945825	0.986796
Adjusted R Square	0.999682	0.989299	0.939053	0.985145
Standard Error	0.334111	3.10826	8.345731	3.470437
Observations	10	10	10	10

Table 5: ANOVA of pseudo- pseudo-second-order -order kinetic model

CRH					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	3161.885	3161.885	28324.68	1.78E-15
Residual	8	0.89304	0.11163		
Total	9	3162.778			
HRH					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	8048.528	8048.528	833.0704	2.25E-09
Residual	8	77.29025	9.661281		
Total	9	8125.818			
SRH					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	9728.139	9728.139	139.6693	2.41E-06
Residual	8	557.2098	69.65122		
Total	9	10285.35			
NRH					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	7200.535	7200.535	597.8557	8.36E-09
Residual	8	96.35147	12.04393		
Total	9	7296.886			

Table 6: ANOVA of pseudo- pseudo-second-order -order kinetic model

CRH								
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	2.927116	0.192284	15.2229	3.44E-07	2.483709	3.370523	2.483709	3.370523
X Variable 1(t)	0.409669	0.002434	168.2994	1.74E-15	0.404055	0.415282	0.404055	0.415282
HRH								
Intercept	21.81116	1.788831	12.19297	1.9E-06	17.68611	25.93621	17.68611	25.93621
X Variable 1 (1/t)	0.653609	0.022645	28.86296	2.25E-09	0.601389	0.705829	0.601389	0.705829
SRH								
Intercept	34.14742	4.80304	7.109543	0.000101	23.07159	45.22325	23.07159	45.22325
X Variable 1 (q/t)	0.718579	0.060803	11.81818	2.41E-06	0.578367	0.85879	0.578367	0.85879
NRH								
Intercept	18.64571	1.997267	9.335615	1.41E-05	14.04001	23.25142	14.04001	23.25142

X Variable 1 (q)	0.618218	0.025284	24.45109	8.36E-09	0.559914	0.676523	0.559914	0.676523

Based at the statistics provided, the first-order kinetic version and the second-order kinetic version had been analyzed for the applicability to explain the adsorption kinetics of 4 materials: CRH, HRH, SRH, and NRH. The regression data for those fashions are as follows:

First-Order Kinetic Model:
- CRH: The R Square is 0.8431. The significance test of the regression equation shows an F-value of 48.36166 and a P-value of 6.65E-05, indicating that the regression model is significant.
HRH: The R Square is 0.9588, appearing higher centrality. The F-value is 209.3537 and the P-value is 1.54E-07, making the model extraordinarily significant.
SRH: The R Square is 0.9698, the most elevated centrality among the various materials. The F-value is 289.0098 and the P-value is 3.79E-08.
NRH: The R Square is 0.9446, with an F-value of 153.385 and a P-value of 5.88E-07.

These results indicate that the first-order kinetic model can satisfactorily portray the adsorption kinetics of these four materials, though the model's explanatory power varies among the different materials. SRH and HRH exhibit stronger explanatory power. The Standard Error indicates that SRH has the smallest measurement error. The F-value and Significance F show that the regression models for all materials are effective at a very high level of significance. The particularly high F-values for CRH and HRH demonstrate the models' effectiveness in capturing data variation.
Second-Order Kinetic Model:
CRH: The R Square is 0.9997, indicating an extremely high explanatory power. The F-value is 28324.68 and the P-value is 1.78E-15, showing the model is highly significant.
HRH: The R Square is 0.9905, with an F-value of 833.0704 and a P-value of 2.25E-09.
SRH: The R Square is 0.9458, with an F-value of 139.6693 and a P-value of 2.41E-06.
NRH: The R Square is 0.9868, with an F-value of 597.8557 and a P-value of 8.36E-09.
The second-order kinetic model shows extremely high explanatory power, particularly for CRH, where the explanatory power is nearly perfect, indicating that the second-order model can more accurately describe the adsorption process.

Analysis of Regression Statistics:
From the regression statistics in Tables 1 and 4, it is evident that for CRH, HRH, SRH, and NRH, the R Square values for the second-order kinetic model (0.999718, 0.986796, 0.990488, 0.945825) are significantly higher than those for the first-order kinetic model (0.843101, 0.944576, 0.958782, 0.9698), indicating that the second-order kinetic model more accurately describes the adsorption processes for these four materials. The R Square values demonstrate that the second-order kinetic model exhibits higher explanatory power across all materials, suggesting that it is more suitable for studying the adsorption kinetics of these particular materials.

ANOVA and Coefficient Analysis:
Agreeing to the ANOVA and coefficient test comes about in Tables 2, 3, 5, and 6, the first-order dynamic demonstrate by and large has littler F-values and bigger P-values for the autonomous variable coefficients, whereas the second-order dynamic demonstrate appears higher F-values and littler P-values, showing way better measurable noteworthiness. Particularly for the hydrophobic adsorbent CRH, the P-value of the autonomous variable coefficient within the first-order show is 6.65E-05, though it is nearly zero within the second-order show, illustrating the predominant expressive capacity of the second-order demonstrate for CRH..

Coefficient Value Analysis:
Tables 3 and 6 show that the first-order show's coefficients are close to zero, and the free factors 'coefficients are also significantly lower. The second-order's independent factors 'mediation and coefficients are larger, and their values are more sensible, as differentiate shows. The second-order demonstration occasionally displays HRH's initial adsorption rate of 1/21.81116 and the ultimate adsorption sum as 1/0.653609, which adjusts more closely with the real circumstance.

4. Conclusion:
This study provides the regression statistics and ANOVA analysis results for pseudo-first-order and pseudo-second-order dynamic models for four distinctive materials (CRH, HRH, SRH, NRH). Based on these information, we assessed the pertinence and precision of the models and summarized the adsorption motor behavior of each material. The adjusted R Square values are also very high, further confirming the model's effectiveness in explaining data variability. The Standard Error indicates that SRH has the smallest measurement error. The F-value and Significance F show that the regression models for all materials are effective at a very high level of significance. The particularly high F-values for CRH and HRH demonstrate the models' effectiveness in capturing data variation. The multiple R and R Square values indicate that the pseudo-second-order kinetic model fits all materials very well, especially CRH and HRH. The adjusted R Square further confirms the high compatibility of the model, particularly for CRH, achieving over 99.97%, demonstrating the model's excellent explanatory power for the data. The Standard Error provides the standard deviation of the measurement error, indicating lower prediction errors for the model. The F-value and Significance F indicate that the regression models for all materials are effective at a very high level of significance. The particularly high F-values for CRH and HRH demonstrate the models' effectiveness in capturing data variation. Based on these data analysis results, it can be concluded that the pseudo-second-order kinetic show is more appropriate for portraying the adsorption dynamic behavior of CRH, HRH, SRH, and NRH. The second-order model provides higher explanatory power and more accurate predictions, making it applicable for future research and applications.

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