Systematic Investigation of pH Influence on Methylene Blue Adsorption Kinetics by Rice Husk: A Comparative Statistical Analysis of Kinetic Models

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Abstract

Addressing the persistent contamination of aquatic ecosystems by synthetic organic dyes, this research investigates the remediation potential of rice husk, a regionally abundant agricultural byproduct, for the sequestration of Methylene Blue (MB). A systematic evaluation was conducted to determine the influence of solution pH, ranging from strongly acidic (pH 2) to highly alkaline (pH 12) on adsorption performance and kinetic behavior. Experimental datasets were subjected to rigorous comparative analysis using linearized pseudo-first-order (PFO) and pseudo-second-order (PSO) models, with statistical validity further scrutinized through Analysis of Variance (ANOVA).

Empirical findings demonstrate that the PFO model exhibits significant limitations under highly acidic conditions (pH 2), yielding a coefficient of determination (R^2) of only 0.1468, likely due to competitive protonation of the adsorbent's surface functional groups. Conversely, the PSO model maintained exceptional statistical robustness across the entire investigated pH range, with R^2 values exceeding 0.99 for pH 4–12. Notably, at pH 12, the PSO model achieved an extraordinary F-value of 15,729.29 and a negligible significance probability (6.62×10^{-16}), indicating near-perfect conformity with the experimental data.

These results underscore that the adsorption mechanism is predominantly governed by chemisorption and surface complexation rather than physical diffusion alone. The progressive deprotonation of the rice husk's lignocellulosic matrix at elevated pH levels significantly enhances the density of negatively charged active sites, thereby intensifying electrostatic attraction toward cationic MB molecules. This study emphasizes the critical importance of statistical precision in kinetic modeling and confirms that untreated rice husk serves as a highly efficient, sustainable biosorbent for cationic dye removal, particularly within neutral and alkaline operational windows.

Keywords: Rice husk; Methylene blue; Adsorption kinetics; pH effect; ANOVA validation

1. Introduction

The utilization of dyes by humankind originated with the extraction of natural colorants from plants, animals, and minerals to color textiles, leather, foodstuffs, cosmetics, and artifacts for aesthetic, symbolic, ritualistic, and bioactive purposes (Yusuf, Shabbir et al. 2017). These natural colorants facilitated intricate applications in fabrics, food enhancement, body adornments, pigments, medicinal formulations, inks, and trade (Yadav, Tiwari et al. 2023). The development of synthetic organic dyes introduced superior brightness, lightfastness, and efficiency expanding uses to industrial textiles, paper, leather, food, cosmetics, pharmaceuticals, and specialty sectors while maintaining interest in sustainable natural systems (Ardila-Leal, Poutou-Piñales et al. 2021).

The extensive utilization of synthetic dyes across industrial sectors, particularly in textile manufacturing, has precipitated substantial environmental pollution through the continuous discharge of voluminous colored effluents laden with complex organic molecules that exhibit remarkable chemical stability and resistance to natural degradation processes, thereby resulting in persistent contamination of aquatic ecosystems (Ardila-Leal, Poutou-Piñales et al. 2021). These recalcitrant compounds not only compromise the aesthetic quality of receiving water bodies but also inflict severe ecological and toxicological hazards by diminishing light penetration, which suppresses photosynthetic activity in aquatic organisms, disrupts food web dynamics, and induces eutrophication, while simultaneously manifesting acute toxicity, mutagenicity, carcinogenicity, and bioaccumulative properties that trigger adverse health outcomes in exposed biota and humans, including respiratory distress, dermal sensitization, nausea, and elevated oncogenic risks (Al-Tohamy, Ali et al. 2022). To mitigate such impacts, a spectrum of pollution prevention and removal technologies has been deployed, ranging from physical processes such as membrane filtration and sedimentation to chemical treatments including coagulation, flocculation, and advanced oxidation, as well as biological approaches employing microbial consortia or enzymatic degradation; although these methodologies afford partial efficacy, they are frequently hampered by elevated operational expenditures, substantial energy requirements, generation of secondary hazardous sludge, or incomplete degradation of persistent chromophores under real-world conditions (Al-Tohamy, Ali et al. 2022). Consequently, the adoption of biomass-derived materials as adsorbents, especially those sourced from abundant agricultural and lignocellulosic wastes such as rice husk, has established itself as the foremost sustainable and economically viable strategy for dye remediation, capitalizing on their inherent porosity, abundant surface functional groups, and renewability to achieve selective high-capacity uptake of cationic species such as methylene blue while minimizing secondary pollution and aligning with circular economy principles (Hongo, Moriura et al. 2021).

The adoption of rice husk and its various derivatives as adsorbents represents a well-established approach in the remediation of dye-contaminated wastewater, capitalizing on the material's natural lignocellulosic matrix and high silica content to provide cost-effective and environmentally benign binding sites for organic pollutants such as methylene blue (Sukmana, Radojčin et al. 2025). Through modifications including carbonization to form biochar or thermal processing to yield rice husk ash, these derivatives exhibit enhanced porosity and surface functionality that significantly improve adsorption kinetics and capacity via mechanisms of electrostatic attraction and pore diffusion (Wazir, Ullah et al. 2023). The present work employs rice husk sourced directly from Taiwan, which confers notable advantages through its regional abundance derived from extensive local rice production, thereby ensuring low procurement costs and seamless integration into Taiwan's waste-to-resource framework, while its untreated form retains optimal surface chemistry that promotes efficient methylene blue uptake without requiring energy-intensive activation processes, fostering sustainable and localized dye pollution mitigation (Huang and Shih 2025).

The pseudo-second-order kinetic model has attained a prominent position in adsorption research as the preferred framework for elucidating the time-dependent uptake of solutes onto solid surfaces, owing to its robust capacity to capture chemisorption-dominated processes and provide reliable correlations with experimental rate data across a wide array of systems (Kostoglou and Karapantsios 2022). Yet the reliance on multiple linearization transformations of its integrated equation has introduced substantial effects on parameter estimation, wherein distinct rearrangements—such as the conventional t/qt versus t plot or alternative expressions—systematically alter error distributions, disproportionately weight data at extended contact times, and yield divergent values for the rate constant and equilibrium capacity that deviate from the underlying nonlinear behavior (Tran 2023). These precision discrepancies arising from linear versus nonlinear regression hold profound importance in adsorption investigations, as they can precipitate misleading mechanistic inferences, compromise the comparability of kinetic parameters across studies, and undermine the predictive utility of derived models unless addressed through rigorous validation protocols that prioritize error-minimizing approaches (Vareda 2023).

The objectives of the present study are to systematically investigate the effects of different pH values on the adsorption performance of rice husk toward methylene blue, concurrently applying the pseudo-second-order kinetic model through its various linear transformation methods to the experimental data so as to evaluate the resultant variations in parameter precision and to emphasize the methodological importance of such transformations in adsorption kinetics, thereby delineating optimal operational conditions for dye uptake while illuminating the precision disparities that linearization can introduce and underscoring their substantial significance for the validity of mechanistic interpretations in adsorption research.

2. Materials and Methods

Adsorption datasets employed throughout this investigation were acquired from previously published experimental studies involving the sequestration of methylene blue (MB) onto rice husk (RH)-based sorbents, which have been extensively recognized as efficient lignocellulosic adsorbents for dye remediation in aqueous systems [(Huang and Shih 2025)]. Rice husk possesses abundant silica, cellulose, hemicellulose, and lignin functionalities that provide numerous active binding sites favorable for cationic dye uptake, thereby making it an environmentally sustainable biosorbent for wastewater purification applications [(Nworie, Nwabue et al. 2019)]. In the batch adsorption analysis, the adsorption capacity at a specified contact duration, denoted as qt (mg g−1), together with the equilibrium adsorption capacity, represented by qe (mg g−1), were determined according to conventional mass-balance relationships widely adopted for adsorption kinetic and equilibrium investigations involving methylene blue and agricultural residues [(Huang and Shih 2025), (Djeribi and Hamdaoui 2008)]. The quantity of dye adsorbed at any reaction interval was calculated using Equation (1), whereas the adsorption amount attained under equilibrium conditions was estimated using Equation (2):

$$q_t = \frac{(C_i - C_t)V}{M} \qquad (1)$$

$$q_e = \frac{(C_i - C_e)V}{M} \qquad (2)$$

where V corresponds to the volume of the dye-containing solution (L), Ci, Ct, and Ce designate the initial concentration, concentration at time t, and equilibrium concentration of methylene blue in the liquid phase (mg L−1), respectively, while M represents the dry mass of rice husk adsorbent introduced into the adsorption system (g). These analytical expressions are broadly accepted for evaluating adsorption performance and kinetic behavior in biosorption systems utilizing lignocellulosic materials for synthetic dye removal from aqueous environments [(Huang and Shih 2025), (Ho and McKay 1999)].

The adsorption kinetics of methylene blue onto rice husk were interpreted using both pseudo-first-order and pseudo-second-order kinetic approaches in order to elucidate the adsorption mechanism and evaluate the influence of contact time on dye uptake behavior. The pseudo-first-order kinetic expression, commonly referred to as the Lagergren model, was employed to describe adsorption systems in which the rate of occupation of adsorption sites is proportional to the number of unoccupied active sites available on the adsorbent surface [(Revellame, Fortela et al. 2020)]. The linearized form of the pseudo-first-order equation was expressed as follows:

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

where q_e(mg g^{-1}) denotes the adsorption capacity at equilibrium, q_t(mg g $^{-1}$) represents the quantity of methylene blue adsorbed at a specified reaction interval t(min), and K_1(min^{-1}) corresponds to the pseudo-first-order adsorption rate constant. This kinetic model has been extensively utilized for evaluating adsorption systems involving lignocellulosic biosorbents and cationic dyes because it provides insight into the initial adsorption behavior and surface diffusion characteristics of the adsorption process [(Etim, Yakubu et al. 2024)]. Nevertheless, adsorption of methylene blue onto rice husk frequently exhibits complex interaction mechanisms involving heterogeneous surface functionalities, thereby necessitating the application of additional kinetic approaches capable of more accurately representing chemisorption-controlled adsorption systems [(Crini 2006)]. Consequently, the pseudo-second-order kinetic model was also applied to investigate the adsorption behavior of methylene blue onto rice husk.

This model assumes that adsorption proceeds predominantly through chemical interactions involving electron exchange, surface complexation, or valence-force interactions between the adsorbate molecules and active functional groups distributed across the biosorbent surface [(Ho and McKay 1999), (Ho and Mckay 1998)]. The linearized pseudo-second-order equation was represented as follows:

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

where K_2(g mg^{-1} min^{-1}) designates the pseudo-second-order adsorption rate constant, while $q_e$and $q_t$retain their previously defined meanings. The pseudo-second-order kinetic approach has been widely recognized as one of the most reliable mathematical models for describing adsorption systems involving agricultural by-products, activated biochar, and silica-rich biomaterials due to its superior capability in characterizing adsorption mechanisms dominated by chemisorption and heterogeneous surface interactions [(Ho, Ng et al. 2000, Vadivelan and Kumar 2005)]. In biosorption systems utilizing rice husk as a low-cost adsorbent for methylene blue removal, adsorption kinetics are strongly affected by the physicochemical characteristics of the adsorbent surface, including the presence of hydroxyl, carboxyl, silanol, and phenolic groups capable of interacting electrostatically with cationic dye molecules [(Sawasdee and Watcharabundit 2023)]. Numerous investigations have demonstrated that pseudo-second-order kinetics generally provide higher correlation coefficients and more accurate prediction of adsorption capacities than pseudo-first-order models because the adsorption process depends substantially on the accessibility and reactivity of active adsorption sites rather than solely on diffusion-controlled transport [(El-Halwany 2010), (Huang and Shih 2025)]. Accordingly, both kinetic models were employed in the present study to comparatively evaluate adsorption behavior under different pH conditions and to identify the dominant adsorption mechanism governing methylene blue sequestration by rice husk.

3. Results and discussion

The statistical analysis of the experimental data was performed using the Analysis ToolPak. The data were fitted to two different linear kinetic equations, with the corresponding regression statistics presented in Tables 1 and 3. The ANOVA results are shown in Tables 2 and 4.

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

	pH2	pH 4	pH 6	pH 8	pH 10	pH 12
Multiple R	0.383169	0.98272	0.981289	0.981539	0.982422	0.96979
R Square	0.146819	0.965738	0.962927	0.963419	0.965153	0.940494
Adjusted R Square	0.046819	0.865738	0.862927	0.863419	0.865153	0.840494
Standard Error	0.114334	0.090617	0.117247	0.123091	0.139007	0.223298
Observations	11	11	11	11	11	11

The regression statistics of the pseudo-first-order kinetic model demonstrated that the adsorption behavior of methylene blue onto rice husk was strongly influenced by the solution pH, indicating substantial variations in the interaction mechanism between the cationic dye molecules and the surface functional groups of the lignocellulosic adsorbent. According to the regression parameters summarized in Table 1, the adsorption system under strongly acidic conditions (pH 2) exhibited extremely poor model applicability, as evidenced by the low coefficient of determination ($R^2 = 0.1468$), weak correlation coefficient (Multiple R = 0.3832), and insignificant F-value with a comparatively high significance probability (Significance F = 0.2221), suggesting that the pseudo-first-order kinetic assumption inadequately represented the adsorption pathway under highly protonated conditions. The low statistical reliability observed at pH 2 indicated that excessive hydrogen ion concentration competitively inhibited the electrostatic attraction between methylene blue and negatively charged adsorption sites on rice husk, thereby suppressing adsorption efficiency and causing substantial deviation from Lagergren first-order behavior [(Ho and McKay 1999), (Huang and Shih 2025)]. This phenomenon has been widely reported for biosorbent-based dye removal systems, where acidic environments reduce the accessibility of active oxygen-containing functional groups such as hydroxyl, carboxyl, and silanol moieties due to proton saturation, ultimately diminishing cationic dye uptake capacity [(Crini 2006), (Foo and Hameed 2010)]. In contrast, the adsorption systems operating within pH 4–12 displayed remarkably high linearity with R^2 values ranging from 0.9405 to 0.9657, confirming that the pseudo-first-order equation adequately described the adsorption kinetics over a broad pH interval except under extremely acidic conditions. The highest regression coefficient was observed at pH 4 ($R^2 = 0.9657$), closely followed by pH 10 and pH 8, indicating that moderately acidic to alkaline conditions significantly enhanced the compatibility between experimental adsorption data and the first-order kinetic assumption. Furthermore, the elevated F-statistics recorded at pH 4–12, particularly at pH 4 (281.8718), pH 10 (276.9679), and pH 8 (263.3622), together with extremely small significance probabilities ($<10^{-6}$), verified the statistical validity and predictive reliability of the regression model. The improved kinetic performance observed under alkaline conditions may be attributed to the progressive deprotonation of rice husk surface functionalities, which generated negatively charged adsorption sites capable of enhancing electrostatic attraction toward positively charged methylene blue molecules [(Nworie, Nwabue et al. 2019), (Gupta 2009)]. Similar adsorption enhancement under alkaline conditions has been documented for agricultural biosorbents containing silica-cellulose matrices, where elevated pH values promote stronger dye–surface interactions through ion exchange, hydrogen bonding, and π–π interactions [(Tran, You et al. 2017)]. Although the pseudo-first-order model demonstrated acceptable fitting characteristics across pH 4–12, the gradual increase in standard error values from pH 4 to pH 12 suggested that kinetic heterogeneity became more pronounced at highly alkaline conditions, likely due to multilayer adsorption or intraparticle diffusion effects contributing simultaneously to the adsorption mechanism [(Weber Jr and Morris 1963)]. Moreover, the relatively lower R^2 value at pH 12 compared with pH 4–10 implied that excessive alkalinity may induce partial instability in the adsorption equilibrium, potentially arising from increased electrostatic repulsion among adsorbed dye molecules occupying densely populated active sites. Nevertheless, the overall kinetic trend clearly revealed that increasing pH substantially improved methylene blue adsorption onto rice husk, confirming that solution pH served as a dominant operational parameter controlling adsorption efficiency and kinetic behavior. The observed enhancement under neutral and alkaline media is consistent with previous investigations reporting superior removal performance of methylene blue using lignocellulosic residues, activated biochar, and silica-rich agricultural waste materials under elevated pH environments due to favorable electrostatic interactions and enhanced accessibility of adsorption sites [(Huang and Shih 2025), (Nworie, Nwabue et al. 2019), (Kyzas and Kostoglou 2014)]. Collectively, the regression analysis demonstrated that the pseudo-first-order kinetic model provided an adequate mathematical representation of methylene blue adsorption onto rice husk under most experimental pH conditions, while strongly acidic environments significantly disrupted adsorption kinetics because of proton competition and reduced surface negativity.

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

pH *2*					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.022495	0.022495	1.72084	0.222058
Residual	10	0.130722	0.013072		
Total	11	0.153217			
pH *4*					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	2.314563	2.314563	281.8718	4.22E-08
Residual	10	0.082114	0.008211		
Total	11	2.396677			
pH *6*					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	3.5706	3.5706	259.7394	6.04E-08
Residual	10	0.137469	0.013747		
Total	11	3.708069			
pH *8*					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	3.990287	3.990287	263.3622	5.68E-08
Residual	10	0.151513	0.015151		
Total	11	4.1418			
pH *10*					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	5.35183	5.35183	276.9679	4.56E-08
Residual	10	0.193229	0.019323		
Total	11	5.545059			
pH *12*					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	7.880667	7.880667	158.0491	5.17E-07
Residual	10	0.498622	0.049862		

Total	11	8.379288			

The analysis of variance for the pseudo-first-order kinetic model revealed that solution pH exerted a substantial influence on the adsorption kinetics of methylene blue onto rice husk, as demonstrated by the pronounced variation in regression significance, residual distribution, and model reliability across the investigated pH conditions. The ANOVA results indicated that the adsorption system at pH 2 exhibited extremely weak statistical validity, with a regression sum of squares (SS = 0.0225), a low F-statistic (1.7208), and a comparatively large significance probability (Significance F = 0.2221), confirming that the pseudo-first-order kinetic equation failed to adequately describe the adsorption process under strongly acidic conditions. This poor statistical agreement suggests that excessive protonation of the rice husk surface suppressed the availability of negatively charged adsorption sites and hindered electrostatic attraction between the cationic methylene blue molecules and the biosorbent surface [(Huang and Shih 2025), (Vadivelan and Kumar 2005)]. Under highly acidic environments, hydrogen ions competitively occupy oxygen-containing functional groups such as hydroxyl and carboxyl moieties, thereby reducing dye accessibility and disrupting adsorption equilibrium behavior, a phenomenon consistently reported in lignocellulosic biosorption systems [(Crini 2006), (Gupta 2009)]. In contrast, the adsorption systems operating within pH 4–12 exhibited exceptionally high regression significance, with F-values ranging from 158.0491 to 281.8718 and significance probabilities below 10^{-6}, indicating that the pseudo-first-order model became statistically reliable once the solution acidity decreased. Among all investigated conditions, pH 4 demonstrated the highest regression significance (F = 281.8718), accompanied by a low residual variance (MS = 0.008211), suggesting that adsorption kinetics at mildly acidic conditions were highly consistent with the assumptions of the Lagergren first-order mechanism. The improved statistical fit observed from pH 4 onward can be attributed to the gradual deprotonation of rice husk surface functionalities, which enhanced the density of negatively charged active sites and facilitated stronger electrostatic interactions with methylene blue molecules [(Farias, Demarco et al. 2022)]. Similar pH-dependent kinetic enhancement has been observed for rice husk-derived adsorbents and other agricultural biomaterials used for dye removal, where moderate alkaline conditions significantly improve adsorption affinity due to increased surface negativity and enhanced accessibility of adsorption domains [(Kaur, Kalpana et al. 2023), (Sukmana, Ballai et al. 2023)]. Furthermore, the continuous increase in regression sums of squares from pH 4 (SS = 2.3146) to pH 12 (SS = 7.8807) reflected a substantial increase in the explainable variation associated with adsorption kinetics, demonstrating that pH elevation intensified the interaction between methylene blue and rice husk. Although the F-value at pH 12 decreased relative to pH 4–10, the model remained highly significant statistically, indicating that the adsorption mechanism under strongly alkaline conditions still followed pseudo-first-order behavior despite possible contributions from secondary diffusion or multilayer adsorption phenomena. The increase in residual mean square at pH 12 (MS = 0.049862) suggested that adsorption heterogeneity became more pronounced under highly alkaline conditions, potentially because of partial saturation of active sites and increased intermolecular interactions among adsorbed dye molecules [(Weber Jr and Morris 1963)]. Nevertheless, the extremely low significance probability at pH 12 confirmed that the model retained strong predictive capability. The ANOVA outcomes therefore demonstrated that pH was a critical operational variable governing the adsorption kinetics of methylene blue onto rice husk, with acidic conditions substantially impairing kinetic conformity and alkaline environments markedly improving adsorption predictability and efficiency. These findings correspond closely with previous studies reporting that methylene blue adsorption onto rice husk, rice husk ash, and silica-rich agricultural residues is strongly favored at neutral and alkaline pH values due to enhanced electrostatic attraction, reduced proton competition, and improved accessibility of adsorption sites [(Farias, Demarco et al. 2022), (Mosoarca, Popa et al. 2021), (Ijaz, Kausar et al. 2025)]. Overall, the statistical interpretation confirmed that the pseudo-first-order kinetic model was unsuitable for describing adsorption behavior under severe acidic conditions but became highly significant and reliable as the solution pH shifted toward neutral and alkaline ranges, thereby emphasizing the dominant role of pH in controlling the adsorption mechanism and kinetic performance of rice husk toward methylene blue removal.

Table3: Regression Statistics of pseudo-second-order kinetic model

	pH *2*	pH *4*	pH *6*	pH *8*	pH *10*	pH *12*
Multiple R	0.968897	0.997742	0.99905	0.998854	0.999267	0.999682
R Square	0.938762	0.995489	0.9981	0.997709	0.998535	0.999365
Adjusted R Square	0.838762	0.895489	0.8981	0.897709	0.898535	0.899365
Standard Error	37.43662	2.903553	1.84485	2.008663	1.589177	0.972511
Observations	11	11	11	11	11	11

The regression statistics obtained from the pseudo-second-order kinetic model demonstrated excellent conformity between the experimental adsorption data and the theoretical kinetic assumptions across all investigated pH conditions, indicating that methylene blue uptake onto rice husk was predominantly governed by adsorption mechanisms associated with chemisorption, surface complexation, and electron-sharing interactions between the dye molecules and active functional groups distributed on the lignocellulosic matrix [(Ho and McKay 1999), (Vadivelan and Kumar 2005)]. The statistical parameters summarized in Table 3 revealed remarkably high coefficients of determination throughout the examined pH range, confirming that the pseudo-second-order equation provided substantially superior predictive capability compared with the pseudo-first-order model. Even under strongly acidic conditions, where the pseudo-first-order model exhibited poor regression performance, the pseudo-second-order model maintained high linearity and statistical reliability, indicating that the adsorption process remained controlled by surface reaction mechanisms despite the inhibitory influence of proton competition. This observation suggests that although excessive hydrogen ion concentration reduced adsorption efficiency, the interaction between methylene blue molecules and rice husk still proceeded through adsorption pathways more accurately represented by second-order kinetics [(Huang and Shih 2025)]. The elevated regression coefficients observed at pH 4–12 further demonstrated that increasing pH significantly enhanced the consistency between experimental adsorption behavior and pseudo-second-order assumptions. Such behavior can be attributed to the progressive deprotonation of hydroxyl, silanol, and carboxylic functional groups on the rice husk surface, which generated greater densities of negatively charged active sites capable of strongly attracting the cationic methylene blue molecules through electrostatic interaction and surface complexation [(Kaur, Kalpana et al. 2023), (Sawasdee and Watcharabundit 2023)]. Similar kinetic characteristics have been extensively reported for rice husk-derived adsorbents and silica-rich agricultural biosorbents employed for dye remediation, where pseudo-second-order models consistently yield higher correlation coefficients than first-order models because the adsorption process involves valence-force interactions rather than simple physical diffusion [(El-Halwany 2010), (A Salem, A Fayed et al. 2018)]. The enhanced agreement of the pseudo-second-order model also implies that adsorption equilibrium was strongly dependent upon the availability of active adsorption sites and the extent of interaction between methylene blue and the heterogeneous surface of rice husk. Furthermore, the relatively low standard error values and high F-statistics observed under neutral and alkaline conditions confirmed the robustness and statistical significance of the regression model, indicating that adsorption kinetics became increasingly stable and predictable as solution pH increased. The strongest kinetic agreement generally occurred within weakly acidic to alkaline conditions, suggesting that these pH environments promoted optimal accessibility of adsorption domains and facilitated rapid surface binding of methylene blue molecules [(Farias, Demarco et al. 2022)]. Under alkaline conditions, the increased concentration of hydroxide ions enhanced surface negativity and reduced competition from protons, thereby intensifying electrostatic attraction and accelerating adsorption rates. This phenomenon has been consistently documented in methylene blue adsorption studies involving rice husk ash, activated biochar, and alkali-treated lignocellulosic materials, where maximum dye removal efficiency and superior kinetic fitting are commonly achieved at pH values ranging from neutral to moderately alkaline conditions [(Sawasdee and Watcharabundit 2023), (Kaykioğlu and Güneş 2016), (Vaz, Pereira et al. 2017)]. Moreover, the superior applicability of the pseudo-second-order model suggested that intraparticle diffusion alone could not adequately explain the adsorption mechanism, and that adsorption was primarily controlled by surface reactions involving functional groups embedded within the rice husk structure. The presence of silica and lignocellulosic constituents within rice husk likely contributed synergistically to adsorption performance through hydrogen bonding, ion exchange, and π–π interactions between aromatic structures of methylene blue and carbonaceous domains of the biosorbent [(Batool, Kanwal et al. 2023)]. Although slight variations in regression parameters were observed among different pH levels, the consistently high statistical agreement demonstrated that the pseudo-second-order model remained highly suitable for describing the adsorption kinetics throughout the investigated experimental conditions. Consequently, the regression analysis confirmed that solution pH substantially influenced the adsorption efficiency and kinetic characteristics of methylene blue removal by rice husk, while the pseudo-second-order model provided the most appropriate mathematical representation of the adsorption mechanism due to its ability to accurately characterize the chemisorption-dominated interactions occurring between the dye molecules and the biosorbent surface.

Table 4: ANOVA of pseudo- pseudo-second-order -order kinetic model

pH *2*					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	214846.1	214846.1	153.2972	5.9E-07

Residual	10	14015	1401.5		
Total	11	228861.1			
pH *4*					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	18604.5	18604.5	2206.776	4.49E-12
Residual	10	84.30622	8.430622		
Total	11	18688.8			
pH *6*					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	17881.7	17881.7	5253.963	9.15E-14
Residual	10	34.0347	3.40347		
Total	11	17915.74			
pH *8*					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	17571.02	17571.02	4354.946	2.13E-13
Residual	10	40.34728	4.034728		
Total	11	17611.37			
pH *10*					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	17213.61	17213.61	6815.963	2.84E-14
Residual	10	25.25484	2.525484		
Total	11	17238.86			
pH *12*					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	14876.4	14876.4	15729.29	6.62E-16
Residual	10	9.457771	0.945777		
Total	11	14885.86			

The ANOVA results derived from the pseudo-second-order kinetic model demonstrated exceptionally strong statistical significance for methylene blue adsorption onto rice husk across the entire investigated pH range, indicating that the adsorption mechanism was predominantly governed by chemisorptive interactions involving surface-active functional groups distributed within the lignocellulosic and silica-rich matrix of the biosorbent [(Ho and McKay 1999), (Huang and Shih 2025)]. The regression analysis presented in Table 4 revealed extremely large F-values together with extraordinarily low significance probabilities, confirming that the pseudo-second-order equation provided outstanding predictive capability and accurately represented the kinetic behavior of methylene blue adsorption under varying pH conditions. At pH 2, although acidic conditions generally suppress adsorption efficiency because of proton competition, the pseudo-second-order model still exhibited remarkably high statistical reliability with an F-value of 153.2972 and a significance level of 5.9×10^{-7}, demonstrating that the adsorption process maintained strong conformity with chemisorption-controlled kinetics even under severe protonation environments. The regression sum of squares at pH 2 reached 214846.1, while the residual variance remained comparatively limited, indicating that the majority of adsorption variability could be effectively explained by the pseudo-second-order kinetic mechanism. This behavior suggests that methylene blue adsorption onto rice husk was not governed solely by physical diffusion but rather involved substantial surface interactions including electron sharing, ion exchange, and electrostatic attraction between the dye molecules and active oxygen-containing functional groups [(Vadivelan and Kumar 2005)]. Similar findings have been extensively reported for lignocellulosic agricultural biosorbents, where pseudo-second-order kinetics frequently dominate adsorption systems involving cationic dyes because adsorption occurs through surface reaction mechanisms rather than simple mass transfer phenomena [(Crini 2006), (Gupta 2009)]. As the solution pH increased from acidic toward alkaline conditions, the ANOVA statistics demonstrated substantial enhancement in regression significance and model conformity. At pH 4, the F-value increased dramatically to 2206.776 with an exceptionally small significance probability of 4.49×10^{-12}, indicating highly reliable kinetic predictability and minimal statistical deviation between experimental and calculated adsorption data. This improvement corresponded closely with the progressive deprotonation of hydroxyl, silanol, and carboxylic groups present on the rice husk surface, which generated increased densities of negatively charged adsorption sites capable of attracting methylene blue molecules through intensified electrostatic interactions [(Kaur, Kalpana et al. 2023)]. The adsorption systems at pH 6, 8, and 10 displayed even greater statistical robustness, with F-values exceeding 4000 and significance probabilities approaching negligible magnitudes, thereby confirming that adsorption kinetics became increasingly ordered and reproducible under near-neutral and moderately alkaline conditions. In particular, the adsorption process at pH 10 exhibited an F-value of 6815.963 with an extremely small residual mean square value of 2.525484, demonstrating superior regression precision and indicating that methylene blue adsorption proceeded through highly stable surface-controlled interactions. Such enhancement under alkaline conditions has been consistently documented in studies involving rice husk ash, activated rice husk biochar, and modified agricultural residues, where elevated pH values improve adsorption performance because deprotonated biosorbent surfaces possess stronger affinity toward positively charged dye molecules [(Sawasdee and Watcharabundit 2023), (Sukmana, Ballai et al. 2023)]. The most statistically significant adsorption behavior was observed at pH 12, where the pseudo-second-order model yielded an extraordinary F-value of 15729.29 and a significance probability of 6.62×10^{-16}, accompanied by an exceptionally small residual variance of 0.945777. These statistical characteristics demonstrated near-perfect conformity between experimental adsorption data and the pseudo-second-order kinetic model, indicating that methylene blue adsorption onto rice husk under strongly alkaline conditions was highly predictable and overwhelmingly controlled by chemisorption mechanisms. The substantial decrease in residual error observed at pH 12 further implied that adsorption heterogeneity became minimized as alkaline conditions promoted greater accessibility and uniformity of adsorption sites. This phenomenon may be attributed to enhanced surface negativity and stronger electrostatic attraction between methylene blue molecules and the rice husk surface, resulting in rapid occupation of energetically favorable adsorption domains [(Farias, Demarco et al. 2022)]. Moreover, the continuously decreasing residual sum of squares from acidic to alkaline conditions suggested that elevated pH values substantially improved adsorption efficiency and kinetic stability. The outstanding applicability of the pseudo-second-order model throughout the entire pH interval also confirmed that intraparticle diffusion was not the sole rate-limiting factor governing adsorption behavior. Instead, the adsorption mechanism likely involved multiple simultaneous interactions including surface complexation, hydrogen bonding, π–π interactions, and ion exchange processes occurring between methylene blue molecules and the heterogeneous rice husk structure [(Weber Jr and Morris 1963)]. These observations are highly consistent with previous investigations demonstrating that pseudo-second-order kinetics provide superior mathematical representation for methylene blue adsorption onto agricultural by-products because the adsorption process fundamentally depends upon the availability and reactivity of surface functional groups [(Ho and McKay 1999, El-Halwany 2010), (Batool, Kanwal et al. 2023)]. Collectively, the ANOVA analysis confirmed that solution pH exerted a dominant influence on the kinetic behavior of methylene blue adsorption onto rice husk, while the pseudo-second-order kinetic model exhibited exceptional statistical significance and predictive reliability under all investigated experimental conditions, particularly within neutral and alkaline environments where adsorption performance and surface interaction intensity were maximized.

4. Conclusion

The findings of this investigation provide compelling evidence for the efficacy of untreated rice husk as a sustainable and high-performance biosorbent for the sequestration of methylene blue from aqueous environments. Through a comprehensive evaluation of adsorption kinetics across a wide pH spectrum, this study underscores the pivotal role of solution chemistry in modulating the interaction between cationic dye molecules and the lignocellulosic surface.

Our empirical data clearly demonstrate that the adsorption capacity and kinetic stability of the system are significantly enhanced under neutral to strongly alkaline conditions. The progressive deprotonation of surface functional groups, specifically hydroxyl, silanol, and carboxylic moieties, creates a high density of negatively charged sites, thereby facilitating robust electrostatic attraction and surface complexation. Conversely, strongly acidic environments (pH 2) were found to severely impair adsorption performance due to intense proton competition for active sites, leading to a marked deviation from theoretical kinetic behaviors.

Statistical validation via ANOVA and regression analysis confirms that the pseudo-second-order (PSO) model provides the most accurate mathematical representation of the adsorption process across the entire investigated pH range. The extraordinary statistical significance observed at pH 12, characterized by a near-perfect coefficient of determination and an unprecedented F-value (15,729.29) further validates that the rate-limiting step is predominantly governed by chemisorption rather than physical diffusion. In contrast, the pseudo-first-order model exhibited significant limitations, particularly in highly acidic media where it failed to provide a reliable predictive framework.

In conclusion, this research highlights that rice husk, an abundant agricultural byproduct in Taiwan, offers a low-cost and ecologically sound alternative to conventional wastewater treatment technologies. The ability to achieve efficient dye removal without energy-intensive activation processes aligns with the core tenets of the circular economy and resource valorization. Future efforts should focus on scaling these laboratory findings to pilot-scale applications and exploring the regeneration potential of the biosorbent to ensure long-term operational sustainability in industrial effluent remediation.

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