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Green Chemistry Meets Colorful Challenges: Biomass Valorization in the Quest for Dye Elimination Red Methyl: A Kinetic, Isothermal, and Proposed Mechanism Study

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Abstract

This study explores the use of walnut shells treated as an adsorbent material for eliminating methyl Red (MR) dye. Initially, the material undergoes characterization through Scanning Electron Microscopy (SEM), revealing its primarily cellulose-rich structure and developed specific surface. Subsequent kinetics analysis indicates that the adsorption process adheres to second-order kinetics, signifying a robust interaction between the dye and walnut shells. Moreover, the application of the Freundlich adsorption model effectively characterizes the adsorption process, affirming the development of a monolayer on the walnut shells' surface. These findings highlight the potential of walnut shells as an economically feasible and environmentally friendly solution for treating water contaminated with dye, achieving an impressive dye removal rate exceeding 84%.

Keywords: *Water Treatment, Dye, Biomass, Mechanism, Environment.*

1. INTRODUCTION

Dye pollution in wastewater is on the rise, driven by industries like textiles, leather, and pulp, compounded by insufficient dye disposal practices. These organic dyes pose significant risks to human, animal, and plant life, resulting in health problems and growth inhibition [1-2]. Ensuring the safe discharge of treated effluent into water bodies requires effective dye removal. Various methods, including membrane filtration, electrochemical treatment, and adsorption, are employed for this purpose [2-6]. Among these methods, adsorption is favored for its simplicity, cost-effectiveness, ease of operation, and minimal generation of secondary pollutants [7, 8]. Commonly used adsorbents for dye removal from wastewater include clay [9], metal oxide adsorbents, and biosorbents. These adsorbents efficiently remove dyes from wastewater due to their abundant functional groups and unique structures. They offer advantages such as substantial surface area, porosity, and specific adsorption characteristics, allowing them to selectively target particular dye types in wastewater. In essence, employing adsorbents presents an effective and straightforward approach to dye removal in wastewater treatment. The adsorption technique on walnut shells has gained attention for its potential in removing pollutants from wastewater. Biomass can interact with dye molecules, facilitating the removal of color contaminants from solutions. The effectiveness of this biosorption process depends on environmental factors such as biomass selection, solution pH, and the nature of the pollutant [10, 11].

In this study, we delved into adsorption kinetics and isotherms after optimizing adsorption parameters to elucidate the adsorption mechanism of dyes in wastewater. Overall, our research aimed to deepen our comprehension of the dye adsorption process in wastewater,

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with a particular focus on adsorption kinetics and isotherms, essential for developing effective wastewater treatment methods and efficiently mitigating dye-related pollution.

2. MATERIALS AND METHODS

2.1 Materials:

The materials employed in this study comprised treated walnut shells and methyl red powder, both procured from Sigma-Aldrich without additional purification. The walnut shells (WS) underwent a thorough cleaning process involving washing with tap water followed by distilled water to eliminate any residual impurities. Following this, the walnut shells were air-dried and further subjected to oven drying at 105°C for 24 hours to ensure the removal of any remaining moisture. The dried samples were subsequently mechanically ground, sieved, and treated with 0.01 M hydrochloric acid (HCl). To prepare a stock solution of methyl red (MR) dye with a concentration of 100 ppm, distilled water was utilized. The concentration of the MR dye in the solution was quantified at 470 nm using a UV/VIS spectrophotometer. This meticulous process ensured the integrity and precision of the experimental setup for the subsequent adsorption studies.

2.2 Caracterization of WST:

For a detailed examination of structural characteristics, we employed FEI Quanta 250 Scanning Electron Microscope (SEM), a state-of-the-art instrument representing the forefront of electron microscopy technology. The SEM holds paramount importance in scientific research, offering the capability to visualize structures at a microscopic scale with exceptional resolution. This microscopic imaging technique is fundamental for our investigation, providing detailed insights into the surface morphology and composition of the materials under scrutiny.

2.3 Batch Experiments:

The kinetic study aimed to assess the adsorption rate of Methyl Red (MR) dye onto a biosorbent derived from raw walnut shell treated (RWT) under optimized conditions. These conditions included a WST (walnut shell treated) concentration of 1 g/L, an initial MR concentration of 50 ppm, and contact times ranging from 4 to 60 minutes. Sample preparation involved mixing the initial MR concentration with 1 g/L of WST and agitating the mixture for varying contact times. Subsequently, at the end of each time interval, a sample was collected, and the residual MR concentration was measured using a UV-VIS spectrophotometer. This analysis provided valuable insights into the adsorption kinetics, elucidating how the MR concentration changes over time in the presence of the RWT biosorbent and thereby revealing the adsorption rate and equilibrium time under the specified optimized conditions.

$$qe = \frac{MR_i - MR_f}{\mathrm{m}} \times V \quad \mathbf{(1)}$$

- MR_i and MR_f denote the initial and final concentrations (mg/L) of MR dye, respectively.
- Capacity (qe, mg/g) of MR removal using the RWT adsorbent

2.4 Adsorption Isotherms :

To validate and enhance the investigation of dye adsorption by the biosorbent, we conducted an examination of the adsorption isotherm at temperatures of 25°C, 35°C, and 45°C. To achieve this, solutions with varying dye concentrations, ranging from 5 to 50 ppm, were

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prepared while maintaining a constant dosage of 0.05 g. The adsorption isotherm for the target product was then generated by plotting the curve:

$$Q_{ads} = f\left(C_{eq}\right) \quad \textbf{(2)}$$

This curve illustrates the relationship between adsorption capacity (Q_ads) and equilibrium dye concentration (C_eq) at different temperatures, providing valuable insights into the biosorption behavior under various thermal conditions.

3. RESULTS AND DISCUSSION

3.1 Caracterization of WST:

Figure 1 illustrates the morphological composition of raw walnut shells at different levels of magnification. Scanning Electron Microscope (SEM) images clearly reveal that the surface of raw walnut shells (WST) exhibits modest level of porosity. These pores facilitate the diffusion of chemical substances in various directions within the WS structure. This diffusion property has the potential to enhance its ability to capture pollutants, making it a promising candidate for pollutant removal applications.

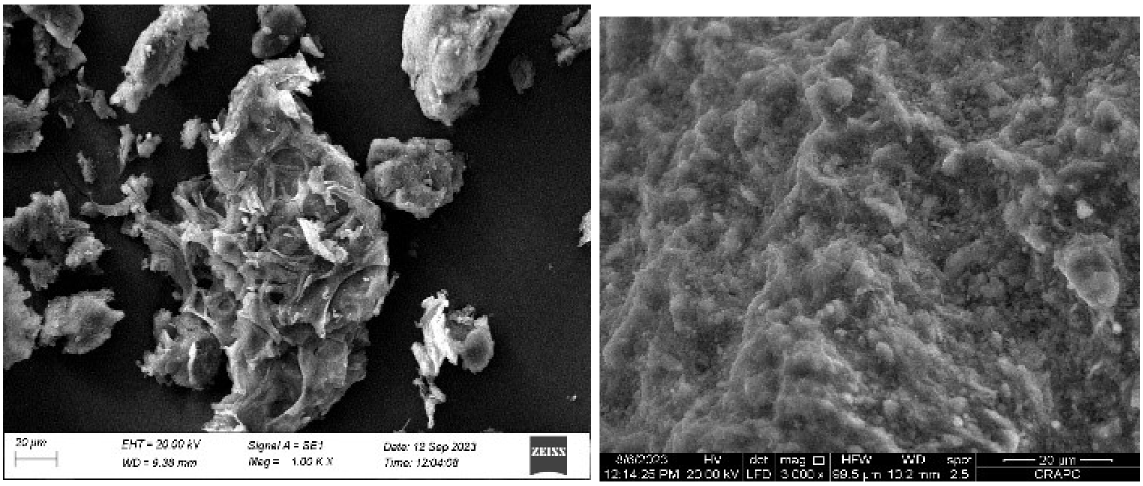

Fig 1: SEM analysis for (a–b) Raw Walnut shell (RWT)

3.2 Kinetic of adsorption

The kinetic data presented in Figure 3 depicts a rapid initial attachment during the early phases of the contact process, reaching equilibrium after approximately 25 minutes. This swift adsorption can be attributed to the initially abundant active sites on the surface of the adsorbent, gradually diminishing over time. At a specific juncture, a pseudo-equilibrium is established, where the rates of adsorption and desorption achieve a balance, resulting in a relatively slower adsorption rate and the manifestation of equilibrium. To ensure the reliable attainment of equilibrium in all adsorption experiments, a 60-minute time period was selected for the duration of contact between the phases. This extended duration allowed for a thorough exploration of the adsorption process, ensuring a comprehensive understanding of the dynamic interaction between the biosorbent and the Methyl Red dye.

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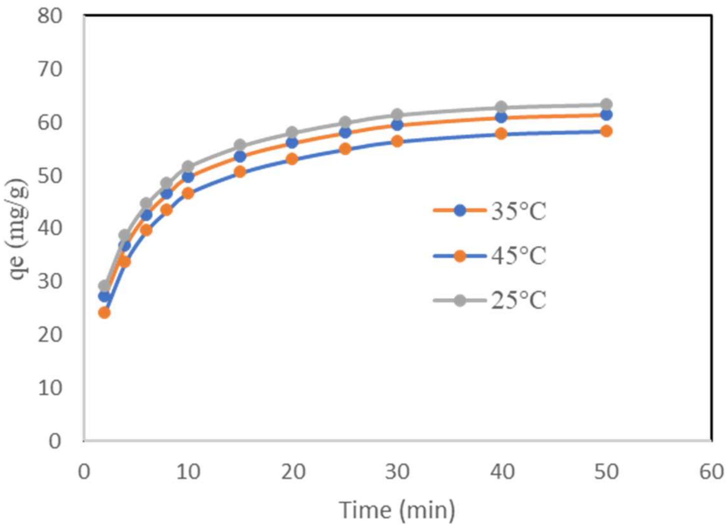

Fig 3: Effect of contact time on adsorption of MR on RWT

3.2.1 Pseudo-first-order kinetic model (PFO)

The Lagergren equation is a representation of pseudo-first-order adsorption in a liquid-solid system. It is expressed as follows [12]:

$$\frac{d(Q)}{dt} = K_1 \times (Q_e - Q_t) \quad \textbf{(4)}$$

The integration of Equation (Eq 5) becomes:

$$\ln(\mathrm{Q_e} - Q_t) = -lnK_1 t + lnQ_e \textbf{(5)}$$

Where :

- Q_t : Adsorbed quantity at time t (mg/g).
- Q_e : Adsorbed quantity at equilibrium (mg/g).
- K_1 : First-order rate constant (min^{-1}).

Figure 4 illustrates the pseudo-first-order kinetic model for the adsorption of MR onto RWT.

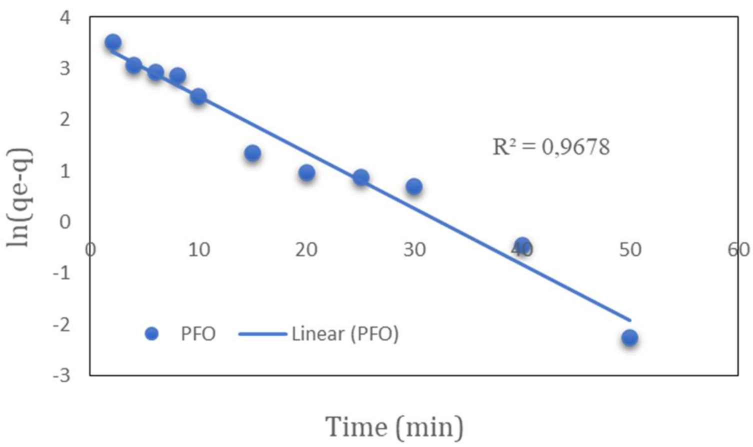

Fig 4: Pseudo first order of adsorption of MR on WST

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3.2.2 Pseudo-second-order kinetic model (PSO)

The equation for this second-order kinetic model can be expressed as [12] :

$$\frac{dQ}{dt} = K_2(Q_e - Q_t)^2 \quad \textbf{(6)}$$

After integration, Equation (Eq 6) becomes :

$$\frac{t}{Q_t} = (\frac{1}{K_2 \times Q_e^2}) + \frac{1}{Q_e} \times t \quad \textbf{(7)}$$

Where :

- K_2 : Second-order rate constant (g·mg⁻1·min⁻1).
- Q_t : Adsorbed quantity at time t (mg/g).
- Q_e : Adsorbed quantity at equilibrium (mg/g).
- t : Time (min).

Figures (5) depict the pseudo-second-order kinetic model for the adsorption of RM onto RWT.

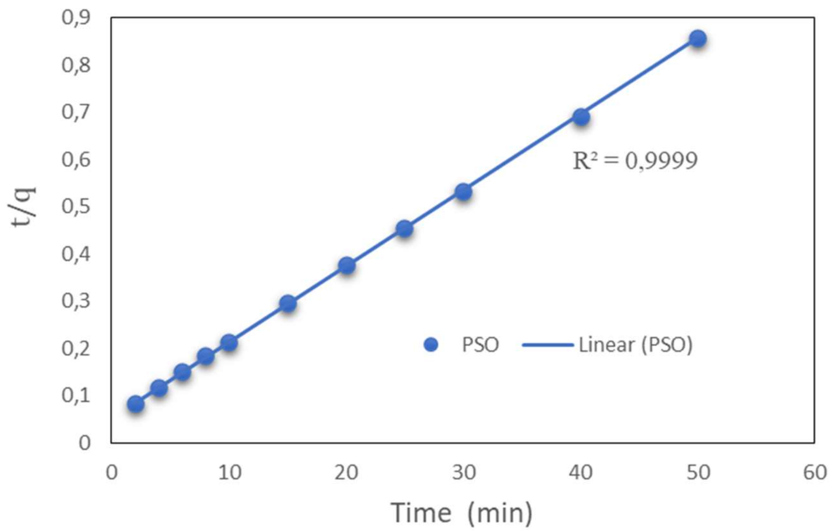

Fig 5: Pseudo second order of adsorption of MR on WST

Moreover, the calculated values from the PSO kinetic model (Q_e, cal, C_al) closely match the experimental observations (Q_e, exp, $C_e$xp). This close correspondence indicates that the PSO kinetic model effectively captures the adsorption behavior of Methyl Red (MR) on WST (walnut shell treated). The model's parameters demonstrate reliability, offering a robust means of predicting both adsorbed quantities and residual concentrations. This emphasizes the accuracy and utility of the PSO kinetic model in characterizing and predicting the dynamic adsorption process of MR on WST.

Table 1: Parameters of kinetic of adsorption of MR on WST

$q_{e.exp}$ (mg.g^{-1})	PFO			PSO		
	$q_{e.cal}$ (mg.g^{-1})	K_1	R^2	$q_{e.cal}$ (mg.g^{-1})	K_2	R^2
28,167	15,86	0,54	0,9678	27,3	0,07	0,9999

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3.3 Isotherms of adsorption of MR on WST

The analysis of adsorption isotherms serves a dual purpose by enabling the computation of the maximum adsorptive capacity of the solid and facilitating the identification of the adsorption mechanism. The experimental findings indicate that the isotherm conforms to Type H, as per Gilles' classification (Gilles 1960) [13]. According to Gilles' classification, there is a discernible increase in adsorption as the concentration of the adsorbate rises, as illustrated in Figure 6.

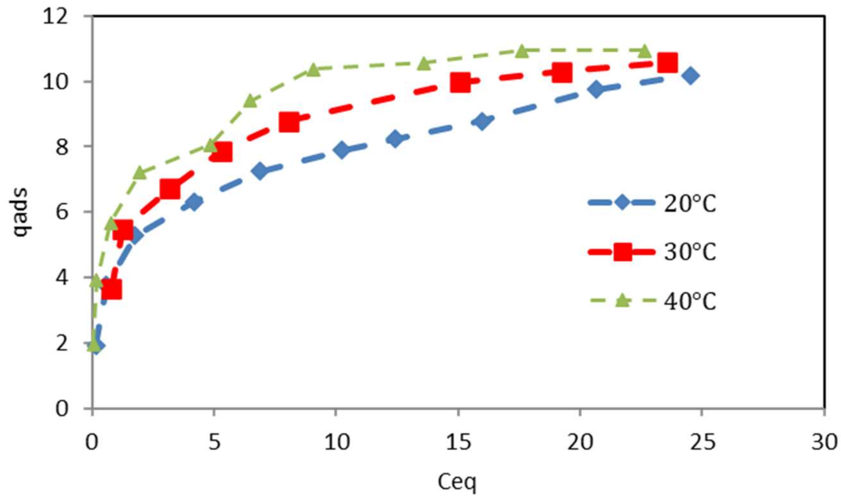

Fig 6: Isotherms of adsorption of MR on WST

3.4 Modeling Adsorption Isotherms

3.4.1 Model of Langmuir

The linear form of the Langmuir equation [8] is:

$$\ln(Q_e) = \ln(K_f) + \frac{1}{n}\ln(C_e \quad \textbf{(8)}$$

- Ce : The solute concentration at equilibrium (mg/l).
- Qe : Represents the amount adsorbed by the solute per unit mass of the adsorbent (mg/g) at equilibrium.
- Qm : The maximum adsorption capacity of the solid (mg/g).
- KL : Empirical constant.

The experimental results of MR removal according to Langmuir are illustrated in Figure 7.

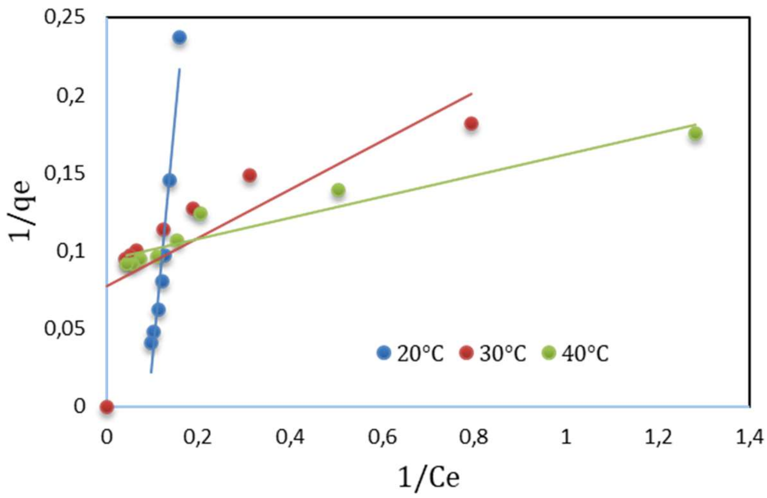

Fig 7 : Langmuir linear form of adsorption of MR on WST

3.4.2 Model of Freundlich

The equation for this model is expressed as follows:

$$\ln(Q_e) = \ln(K_f) + \frac{1}{n}\ln(C_e) \quad \textbf{(9)}$$

Where :

- k_f : Freundlich constant characterizing the adsorption capacity of the solid;
- 1/n : Freundlich constant characterizing the affinity of the product for the adsorbent.

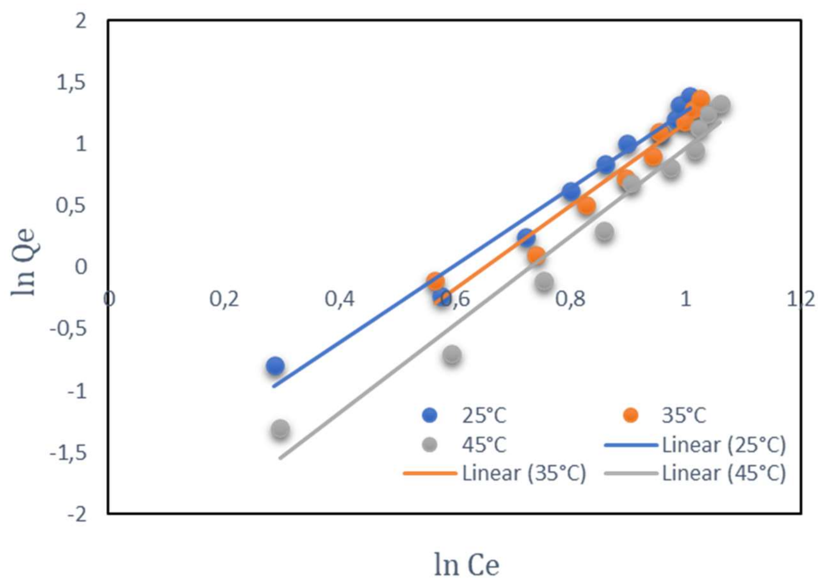

Fig 8 : Freundlich linear form of adsorption of MR on WST.

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Table 2: Adsorption Parameters for MR on WST

	Langmuir			Freundlich		
T°C	**q_m (mg/g)**	**K_L (mg/g)**	**R^2**	***n***	**K_F (mg/g)**	**R^2**
25	19,76	0,09	0,8879	0,76	3,962	0,9781
35	13,33	59,25	0,9226	0,74	5,248	0,9453
45	10,75	1,367	0,9099	0,7	6,095	0,9672

Based on the correlation coefficients (R^2) related to the linearity of the adsorption isotherms for the studied models, we can conclude that the Langmuir model is the most likely to characterize the adsorption of MR on WST.

Adsorption constant (K) : a. A high value of K indicates strong affinity between the solute and the solid surface, leading to more efficient adsorption. b. A low value of K suggests weak affinity between the solute and the solid surface, resulting in less effective adsorption.

3.5 The proposed mechanism for the adsorption of MR on WST

The adsorption of the dye onto the mesoporous and macroporous material primarily composed of cellulose is a complex process involving both physical and chemical interactions. The kinetics of this reaction is second-order, indicating that the reaction rate depends on the square of the dye concentration. Cellulose, being the main component of the material, plays a significant role in facilitating these interactions through hydrogen bonding, pi-π interactions, and electrostatic interactions. However, further research is essential to confirm this adsorption mechanism and understand the specific interactions occurring during this process in detail.

4. CONCLUSION

In conclusion, the study on the adsorption of methyl red onto walnut shells treated (WS) has yielded promising results.

The kinetic analysis has revealed that the adsorption process of MR onto walnut shells follows a second-order kinetics, indicating a stronger interaction between the dye and the adsorbent. Furthermore, the Langmuir adsorption model has been successfully employed to describe the MR adsorption, confirming the formation of a monolayer on the surface of the walnut shells.

It is crucial to emphasize that the MR removal rate reached an impressive 84%, demonstrating the efficiency of walnut shells as an adsorbent material for MR decolorization. This high performance underscores the potential of walnut shells as an economical and environmentally friendly alternative for treating water containing dyes.

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