Investigating Biomass Valorization for Synthetic Dye Red Congo Elimination: Kinetics, Isothermals, and Thermodynamics Study

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Abstract

This study delves into the utilization of unprocessed raw walnut shells as an eco-friendly biosorbent for the removal of Congo Red (CR) dye from water. The research investigates the adsorption capabilities of walnut shells in their natural state and incorporates a comprehensive thermodynamic analysis.

Characterization utilizing Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) unveiled the predominantly cellulose-rich structure of raw walnut shells. Kinetic analysis revealed that the adsorption process adheres to second-order kinetics, highlighting a robust interaction between CR dye and walnut shells. The application of the Freundlich adsorption model effectively described the adsorption process, confirming monolayer formation on the walnut shell surface.

Furthermore, our thermodynamic study demonstrated that the adsorption process is exothermic and spontaneous, adding an essential dimension to the understanding of this environmentally benign dye removal method. Impressively, the biosorbent achieved a dye removal rate exceeding 92%. These findings underscore the economic and environmentally friendly potential of unprocessed raw walnut shells for the treatment of dye-contaminated water. This research not only contributes to sustainable materials but also addresses the pressing issue of dye pollution through a practical and eco-conscious approach.

Keywords: pollution, dye, biosorption, walnut shell, water, environment, Congo red.

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I Introduction

Wastewater pollution from organic dyes is escalating due to industries such as textiles, leather, and pulp, along with inadequate dye disposal practices [1]. These dyes have detrimental impacts on humans, animals, and even plant life, causing health problems and growth inhibition [2]. To ensure the safe discharge of treated effluent into water bodies, effective dye removal is imperative. Various methods, such as membrane filtration, electrochemical treatment, and adsorption, are employed for this purpose [2, 3, 4, 5, 6]. Among these methods, adsorption is

favored for its simplicity, cost-effectiveness, ease of operation, and minimal generation of secondary pollutants [7, 8]. A range of adsorbents, including clay [9], metal oxide adsorbents, and biosorbents, are commonly used for dye removal from wastewater.

These adsorbents are highly efficient in eliminating dyes from wastewater, owing to their abundant functional groups and distinctive structures. They offer multiple advantages, including substantial surface area, porosity, and specific adsorption characteristics that enable them to selectively target particular dye types in wastewater. In summary, employing adsorbents constitutes an effective and streamlined approach for dye removal in wastewater treatment.

The technique of biosorption on walnut shells has garnered attention due to its potential for pollutant removal from wastewater. Biomass possesses the capability to interact with dye molecules, leading to the removal of color contaminants from solutions. The effectiveness of this biosorption process is influenced by several environmental factors such as the choice of biomass, solution pH, and the nature of the pollutant present [10, 11].

In this study, we investigated the biosorption kinetics, isotherms and thermodynamic study after optimizing the adsorption parameters to elucidate the adsorption mechanism of dyes present in wastewater.

Overall, this research aimed to deepen our understanding of the dye biosorption process in wastewater, with a focus on adsorption kinetics and isotherms, crucial for the development of effective wastewater treatment methods and the efficient reduction of dye-related pollution.

II Materials and Methods

II.1 Méterals:

The materials employed in this study included raw walnut shell powder, Congo red powder. All chemicals were procured from Sigma-Aldrich and were used without additional purification. The walnut shells (RWS) under went thorough was hing with tap water followed by distilled water to eliminate any residual impurities. Subsequently, they were air-dried and further dried in an oven at 105°C for 24 hours to remove any remaining moisture. The dried sample wasthen mechanically ground and sieved to obtain particles within the size range of 250 to 315 µm for use in the adsorption experiments.

To create a stock solution of CR dye with a concentration of 100 ppm, distilled water was utilized, and the pH was adjuste dusing 0.1 N solutions of hydrochloric acid and sodium hydroxide. The concentration of the remaining CR dye was quantified at 535 nm using a UV/VIS spectrophotometer (PerkinElmer Lambda 25).

II.2 Caracterization of WS:

Structural analysis through X-ray powder diffraction (XRD) was conducted using the EMPYREAN X-ray diffraction instrument. The instrument covered a scanning range from 5 to 90 degrees (2θ).

In our research, we utilized the state-of-the-art FEI Quanta 250 Scanning Electron Microscope (SEM), which is at the forefront of electron microscopy technology. The SEM is a fundamental tool in scientific research as it provides the capability to visualize structures at a microscopic scale with exceptional resolution.

II.3 Batch Experiments:

The kinetic study was conducted to evaluate the adsorption rate of CR dye (Congo Red) onto raw walnut shell (RWS) biosorbent under optimized conditions, which included a RWS concentration of 2 g/L, an initial CR concentration of 30 ppm, and contact times ranging from 4 to 60 minutes. To prepare the samples, the initial CR concentration was mixed with 2 g/L of WS and agitated for varying contact times. At the end of each time interval, a sample was collected, and the residual CR concentration was measured using a UV-VIS spectrophotometer. This analysis provided insights into the adsorption kinetics, illustrating how the CR concentration changes over time in the presence of the RWS biosorbent, thus shedding light on the adsorption rate and equilibrium time under these optimized conditions.

The efficiency (%) and capacity (qe, mg/g) of CR removal using the RWS adsorbent were determined using the following equations (1) and (2):

These equations allow for the quantification of the efficiency and adsorption capacity of CR removal by the RWS adsorbent, providing valuable data for the assessment of the biosorption process.Top of Form

$$R\% = \frac{CR_i - CR_f}{SD_i} \times 100 \qquad (1)$$

- CRi and SDf denote the initial and final concentrations (mg/L) of CR dye, respectively.

II.4 Adsorption Isotherms :

To validate and complement the investigation of dye adsorption by the biosorbent, we conducted an examination of the adsorption isotherm at temperatures of 25°C, 35°C, 45°C. To accomplish this, we created solutions with different dye concentrations, spanning from 5 to 50 ppm, while maintaining a constant dosage of 0.05 g. The adsorption isotherm for the target product was generated by plotting the curve:

$$Q_{ads} = f(C_{eq}) \qquad (2)$$

III Results and discussion:

III.1 Caracterization of RWS:

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 (RWS) 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.

The X-ray diffraction (XRD) pattern exhibited by raw walnut shells in Figure 2 typically reveals two prominent peaks: a major peak located at approximately 21,45 degrees and a smaller peak around 29,27 degrees. The significant peak at 21,45 degrees signifies the presence of cellulose, a crystalline component commonly found in the cell walls of plants, including walnut shells. Meanwhile, the minor peak at 29,27 degrees suggests the possible presence of other crystalline constituents, such as lignin or hemicellulose, which are also essential components of the cell wall structure. These observations indicate that raw walnut shells consist of a mixture of crystalline materials, with cellulose being the primary component.

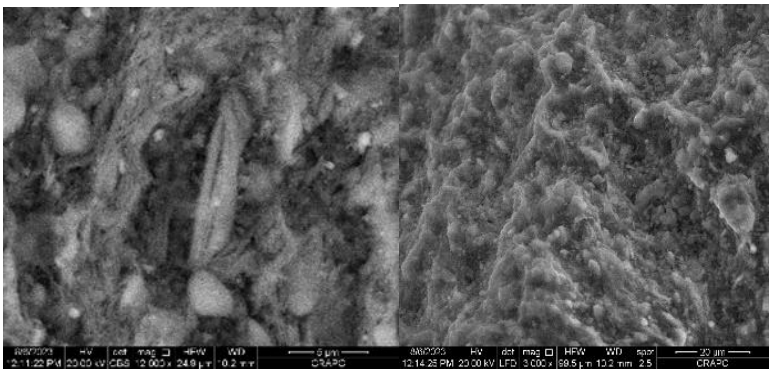

Figure. 1 SEM analysis for (a–b) Raw Walnut shell (RWS).

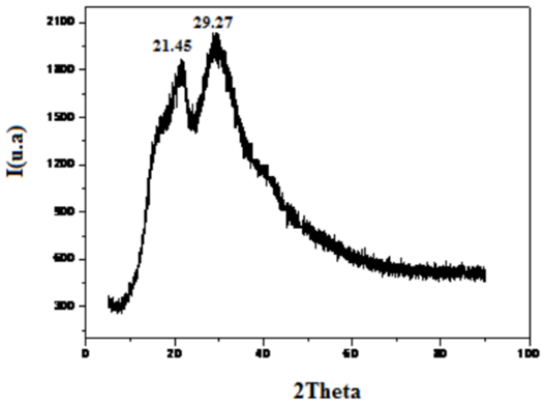

Figure. 2 XRD patterns of Raw Walnut shell (RWS).

III.2 Kinetic of biosorption:

The kinetic data presented in Figure 3 illustrates a swift initial attachment during the early stages of the contact process, with equilibrium being achieved after approximately 30 minutes of contact. This rapid adsorption can be attributed to the initial abundance of active sites on the surface of the adsorbent, which gradually diminishes as time progresses. At a certain point, a pseudo-equilibrium is established, where the rates of adsorption and desorption reach a balance, resulting in a relatively slower adsorption rate and the appearance of equilibrium. To ensure

equilibrium was reliably reached in all adsorption experiments, a 60-minute time period was selected for the duration of contact between the phases.

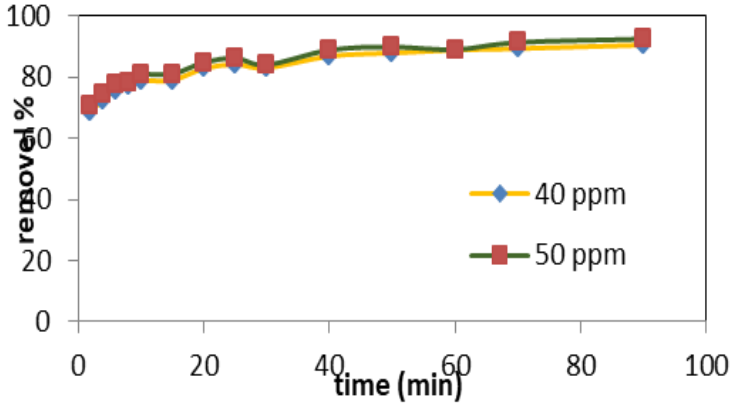

Figure. 3 Effect of contact time on adsorption of CR on RWS.

III.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 [12-15]:

$$\frac{d(Q)}{dt} = K_1 \times (Q_e - Q_t) \qquad (3)$$

The integration of Equation (Eq 5) becomes:

$$\ln(Q_e - Q_t) = -lnK_1 t + lnQ_e \qquad (4)$$

Where:

- Qt: Adsorbed quantity at time t (mg/g).
- Qe: Adsorbed quantity at equilibrium (mg/g).
- K1: First-order rate constant (min^{-1}).

figure 4 illustrates the pseudo-first-order kinetic model for the adsorption of CR onto RWS.

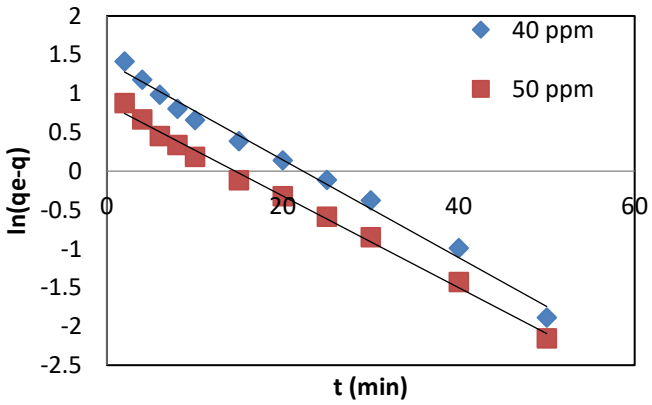

Figure.4: Pseudo-first-order model for the adsorption of CR onto RWS.

III.2.2. Pseudo-second-order kinetic model (PSO)

The equation for this second-order kinetic model can be expressed as [12-15]:

$$\frac{dQ}{dt} = K_2(Q_e - Q_t)^2 \qquad (5)$$

After integration, Equation (Eq 5) becomes:

$$\frac{t}{Q_t} = (\frac{1}{K_2 \times Q_e^2}) + \frac{1}{Q_e} \times t \qquad (6)$$

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 BM onto CN.

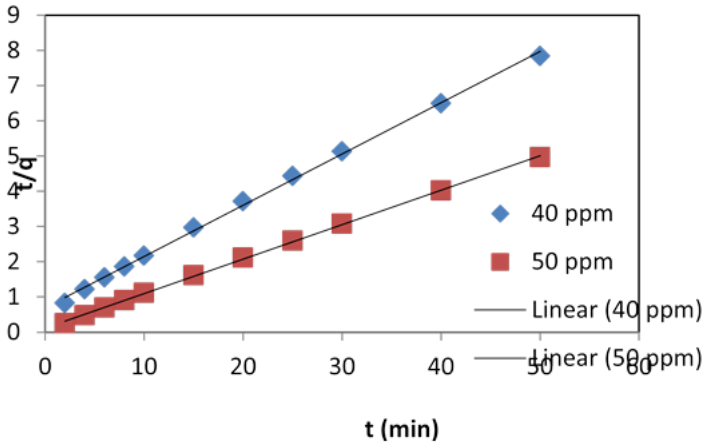

Figure. 5: Pseudo second order of biosorption of CR on RWS.

Table 1: Kenitic parameters of biosorption of CR onto RWS

Kinetic equation	PFO			PSO		
Parameters	R2	K1 (min-1)	qe (ppm)	R2	K2	qe (g.mg-1)
RWS	0.783	11,63	3,38903* 103	O,996	-77506,805	0,0024728

III. 3 Isotherms of adsorption of CR on RWS

The determination of adsorption isotherms enables us to compute the maximum biosorptive capacity of the solid and also facilitates the identification of the biosorption mechanism.

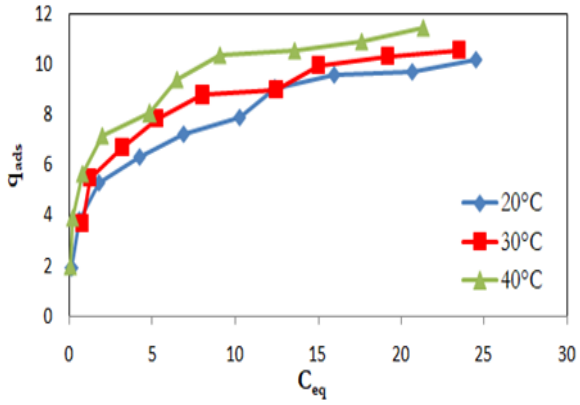

Figure. 6 Isotherms of adsorption of CR on RWS.

The experimental results obtained demonstrate that the isotherm follows Type H, in accordance with Gilles' classification (Gilles 1960) [16]. Gilles' classification implies an increase in adsorption as the adsorbate concentration rises, as shown in Figure 6.

III.4 Modeling Adsorption Isotherms

III.4.1. Model of Langmuir

The equation for this model is expressed as follows:

$$\frac{1}{Q_e} = \frac{1}{(K_L + Q_m + C_e)} + \frac{1}{Q_m} \qquad (7)$$

Where:

C_e: The solute concentration at equilibrium (mg/l).

Q_e: Represents the amount adsorbed by the solute per unit mass of the adsorbent (mg/g) at equilibrium.

Q_m: The maximum adsorption capacity of the solid (mg/g).

K_L: Empirical constant.

The linear form of the Langmuir equation [17] is:

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

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

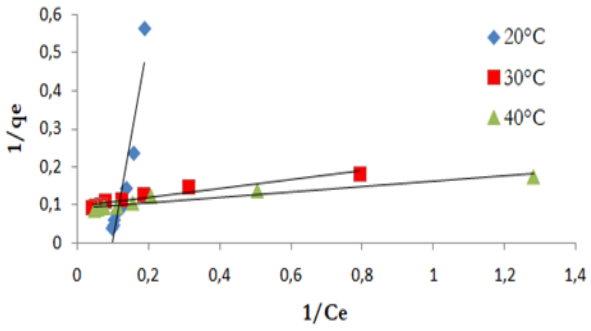

Figure. 7 : Langmuir linear form of adsorption of CR on WS.

III.4. 2 Model of Freundlich

The equation for this model is expressed as follows [18]:

(9)

Where:

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

The linear form of the Freundlich isotherm is typically represented by the equation:

$$\ln(Q_e) = \ln(K_f) + \frac{1}{n}\ln(C_e) \qquad (10)$$

Table 2: Adsorption Parameters for CR on WS.

Langmuir				Freundlich		
T°C	q_m (mg/g)	K_L (mg/g)	R^2	n	K_F (mg/g)	R^2
20	1,976	0,79	0,88	0,76	2,962	0,95
30	13,33	0,25	0,88	0,74	4,268	0,99
40	10,75	1,367	0,9	0,7	6,098	0,96

Based on the correlation coefficients (R2) related to the linearity of the adsorption isotherms for the studied models, we can conclude that the Freundlich model is the most likely to characterize the adsorption of CR on RWS.

Interpreting the results of the Freundlich equation relies on the values of the parameters K and n. Here are some general interpretations [19]:

Freundlich exponent (n) value: When n < 1, it indicates that adsorption is favored at low solute concentrations, implying that adsorption decreases as the solute concentration in the liquid phase increases.

Adsorption constant (K): a. A high K value signifies a strong affinity between the solute and the solid surface, resulting in more efficient adsorption.

It's important to note that the Freundlich model is an empirical approximation of adsorption and does not account for specific interactions between the solute and the solid surface. Consequently, its applicability is often limited to systems where interactions are primarily of a physical nature rather than chemical.

IV. Thermodynamic parameters :

The effect of temperature on the biosorption of CR onto RWS was carried out in temperatures 20°C, 30°C and 40°C at an initial concentration of 40 ppm and fixed bisorbant dose of 2g/L. The results found that the adsorption capacity increased with decreasing temperature which indicates that the

adsorption process is exothermic in nature. The equilibrium partition coefficient (Kc) is calculated as follows [2]:

$$K_c = \frac{C_s}{C_e} \qquad (11)$$

The thermodynamic parameters such as change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated from the following equations and listed in Table 2.

$$\Delta G = -RT\ln K_c \qquad (12)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (13)$$

Where R is the gas constant (8.314 J/mol K), Cs and Ce the equilibrium concentrations of CR in the adsorbent ppm and solution ppm, respectively,
T is the solution temperature (K). ΔH and ΔS were calculated from the slope and intercept of the plot of lnKc versus 1/T as shown in Figure. 8.

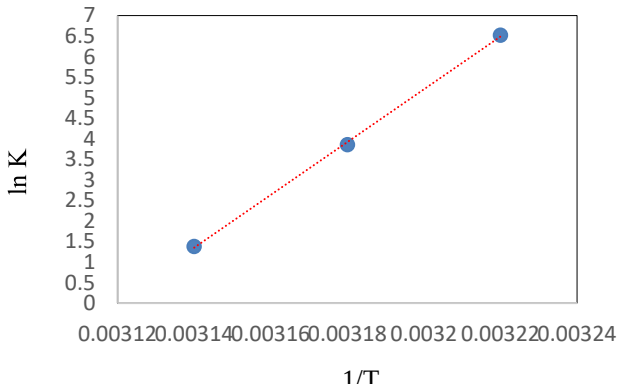

Figure .8: Van't Hoff plots of CR onto RWS.

Table 3 :Thermodynamic data for the biosorption of CR onto RWS

Temperature K	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol)	R^2
293	-3,594			
303	-2,897	-18,639	69,937	0,9999
313	-2,195			

The negative values of ΔG and negative values of ΔH indicate that the biosorption of CR onto RWS is spontaneous and exothermic process. The values of ΔH are high enough to ensure the strong interaction between CR and RWS. The positive values of ΔS indicate that the randomness increased at the solid–solution interface during the adsorption of CR onto RWS . The biosorption capacity of raw walnut shell decreased at higher temperatures [21].

V. Conclusion

In summary, the investigation into the adsorption of Congo Red (CR) onto raw walnut shells (RWS) has delivered promising outcomes.

The kinetic analysis unveiled that the CR adsorption onto raw walnut shells adheres to second-order kinetics, signifying a robust interaction between the dye and the adsorbent. Moreover, the Freundlich adsorption model proved effective in describing the CR adsorption process, confirming the creation of a monolayer on the surface of the raw walnut shells.

It is crucial to highlight that the removal rate of CR reached an impressive 92%, showcasing the efficacy of walnut shells as an adsorbent for CR decolorization. This remarkable performance underscores the potential of walnut shells as an economical and environmentally friendly alternative for treating dye-contaminated water.

Regarding the thermodynamic results, the negative values of ΔG and negative values of ΔH indicate that the biosorption of CR onto RWS is a spontaneous and exothermic process. The high ΔH values suggest a strong interaction between CR and RWS. Additionally, the positive values of ΔS suggest increased randomness at the solid-solution interface during CR adsorption onto RWS. However, it's noteworthy that the biosorption capacity of raw walnut shells decreases at higher temperatures.

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