Thermodynamic, Kinetics and Equilibrium Study of Methylene Blue Adsorption on Red Gram Seed Husk as Bio Adsorbent from Aqueous Solution

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Abstract: ***This study investigates the thermodynamic, kinetic and equilibrium properties of methylene blue adsorption onto red gram seed husk (RGSH) as a bio-adsorbent from aqueous solutions. The effects of various parameters such as initial dye concentration, adsorbent dose, contact time and temperature were evaluated to determine the optimal conditions for adsorption. Adsorption kinetics was determined using pseudo-first and pseudo-second order models, and equilibrium data were analyzed using Langmuir and Freundlich isotherm models. The results show that RGSH can effectively remove methylene blue from aqueous solutions with a high adsorption capacity of 357.83 mg/g. The adsorption process was found to follow a pseudo-first-order model and the Langmuir isotherm provided a better fit, suggesting a monolayer adsorption mechanism. Thermodynamic parameters including free energy change (∆G°), enthalpy change (∆H°) and entropy change (∆S°) were determined, indicating that the adsorption process is spontaneous and exothermic in nature. The study concludes that RGSH is a promising low-cost bio-adsorbent for the removal of methylene blue from wastewater.***

Keywords: Kinetics, Equilibrium, Thermodynamics, Methylene blue,red gram seed husk, Bio-adsorbent

1. Introduction

Water pollution is one of the major environmental problems that has become a global problem due to rapid industrialization and urbanization. The textile industry is one of the major contributors to water pollution as it produces huge amounts of wastewater containing various types of dyes, chemicals and other pollutants. Dyes are one of the main sources of water pollution and their discharge into water bodies can have harmful effects on human health and the environment. Among various dyes, methylene blue (MB) is commonly used in the textile industry and has become a major source of water pollution. MB is a cationic dye and is highly toxic and carcinogenic in nature, posing a serious threat to human health and the environment. Therefore, it is necessary to remove MB from wastewater before it is released into the environment. Common techniques used to remove heavy metal ions from industrial wastewater have been reported in the literature, which include ion exchange, reverse osmosis, electrocoagulation, chemical precipitation, neutralization, and adsorption [1]. Among the various methods available to remove dyes from wastewater, adsorption is considered to be an effective and environmentally friendly method. The use of cheap and sustainable adsorbents such as agricultural waste and biomass has gained considerable attention in recent years due to their abundance, low cost, and high adsorption capacity. A literature survey shows that so many low-cost alternative adsorbents have been proposed in recent decades, which include bamboo [2], oak wood biochar [3], pine wood, pig manure and cardboard [4], cedrelaodrorata seeds [5], green gram [6]; neem leaves [7], gram seed husk, [8], cucumber peel [9], palm kernel Wrap [10], red gram seed husk (RGSH) is a by-product of the pulse industry and is considered as a cheap and environmentally friendly adsorbent due to its abundant availability , high porosity and favorable surface properties, which makes it an effective adsorbent for removing dyes from wastewater. In this regard, this study aimed to investigate the kinetics, equilibrium and thermodynamics of MB adsorption onto RGSH as a bio-adsorbent from aqueous solutions.

Several studies have reported the use of agricultural waste as adsorbents for the removal of dyes from wastewater. However, limited research is available on the use of red gram husks as an adsorbent for MB removal from wastewater. The present study is therefore an attempt to fill this gap in the literature [11].

2. Materials and Methods

Preparation of adsorbent:
Red gram seedshusk (RGSH) was obtained from the local market. The RGSH was thoroughly washed with distilled water to remove any impurities and completely dried in the shade. The dried RGSH was ground into a fine powder using a grinder and sieved through various sieves. The resulting RGSH powder was stored in an airtight container until further use.

Preparation of adsorbate:
Methylene blue (MB) was purchased from Sd. Fine Chemicals Pvt. Ltd. Mumbai (India) and used without further purification. A stock solution of 1000 mg/L was prepared by dissolving the required amount of MB in distilled water. Working solutions of different concentrations (50, 100, 150, 200 and 250 mg/L) were prepared by diluting the stock solution with distilled water. The concentration of the MB solution was determined spectrophotometrically from the calibration curve.

Batch Experiments:
Batch adsorption experiments were conducted to investigate the adsorption kinetics, equilibrium and thermodynamics of

methylene blue (MB) onto red gram peels. Adsorption experiments were performed in 250 ml Erlenmeyer flasks containing 50 ml MB solution of known concentration. A predetermined amount of bio-adsorbent (1 g) was added to the flask and the contents were shaken for predetermined times (5, 10, 15, 20, 25, 30, and 35 minutes) at room temperature. After shaking, the flask was centrifuged for 10 min to separate the adsorbent from the solution. The pH of the solution was adjusted using 0.1 N NaOH and 0.1 N HCl solutions. The concentration of MB in the supernatant was determined using a UV-Vis spectrophotometer at 570 nm.

The concentration of adsorbed MB (mg/g) was calculated using the formulas given by Vanderborght and Van Griekenm [12] and then the kinetic adsorption parameters were calculated.

$$q = \frac{V(Co-Ct)}{M} \quad (1)$$

Where q is the concentration of MB adsorbed from the solution (mg/g), Co is the concentration of MB before adsorption (mg/L) and Ct is the concentration of MB after adsorption. V is the volume of MB solution (L) and M is the mass of RGSH adsorbent (gm).

The adsorption percentage of MB dye was calculated according to the following equation;

$$\text{Percentage adsorption} = \frac{(C_0 - C_e)}{C_0} * 100 \quad (2)$$

Where, C_0 and C_e are the initial and equilibrium concentrations respectively.

3. Results and Discussion

Effect of contact time and initial concentration:

The contact time is a decisive factor that determines the efficiency of the adsorption process. It refers to the time the adsorbent and adsorbate are allowed to interact with each other.

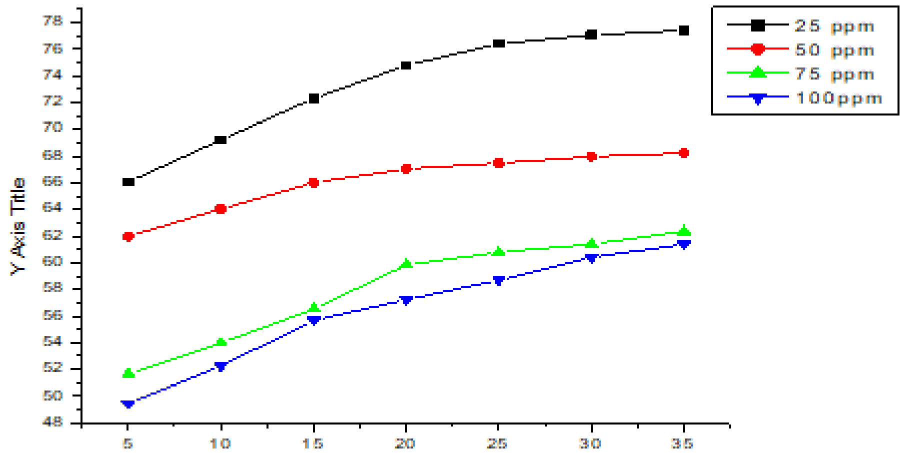

Fig.1: Effect of contact time with different concentration of MB dye adsorption on RGSH adsorbent. [Adsorption dose=1g,Volume=50mL, Temp=298.5K,pH=7]

The adsorption percentage of MB dyes increased with increasing contact time due to the larger available surface area of the adsorbent. The maximum adsorption efficiency was 77.40% for MB after 35 minutes. The study found that the adsorption process was rapid in the initial stages and the optimum contact time for maximum dye removal was 35 minutes. The authors suggested that after 35 min the adsorption rate slowed down due to saturation of the adsorbent surface.

In conclusion, it was found that the optimal contact time for the adsorption of methylene blue on RGSH as a bio-adsorbent from an aqueous solution is 35 minutes. The adsorption process is fast in the initial stages and the adsorption rate slows down after the optimal contact time due to saturation of the adsorbent surface. Similarly, a study investigated the adsorption of MB onto red gram peels as a bio-adsorbent [13].

It was observed that the adsorption capacity of red gram peel for M dye decreased as the initial concentration of the dye solution increased. The authors reported that the maximum adsorption capacity (74.40%) was observed at an initial concentration of 25 mg/L, while at higher concentrations (100 mg/L), the adsorption capacity (61.38%) decreased due to saturation of the adsorbent surface. [14].

Effect of adsorbent dose:

Adsorbent dosage is an important factor that affects the adsorption efficiency of MB from aqueous solutions using bio-adsorbents such as RGSH. Adsorption of MB solution using RGSH in different dosages of adsorbent from 0.5 g to 1.0 g/50 mL solution while maintaining MB concentration at 100 mg/L. at pH 7.0. The results are shown in Fig. 2:

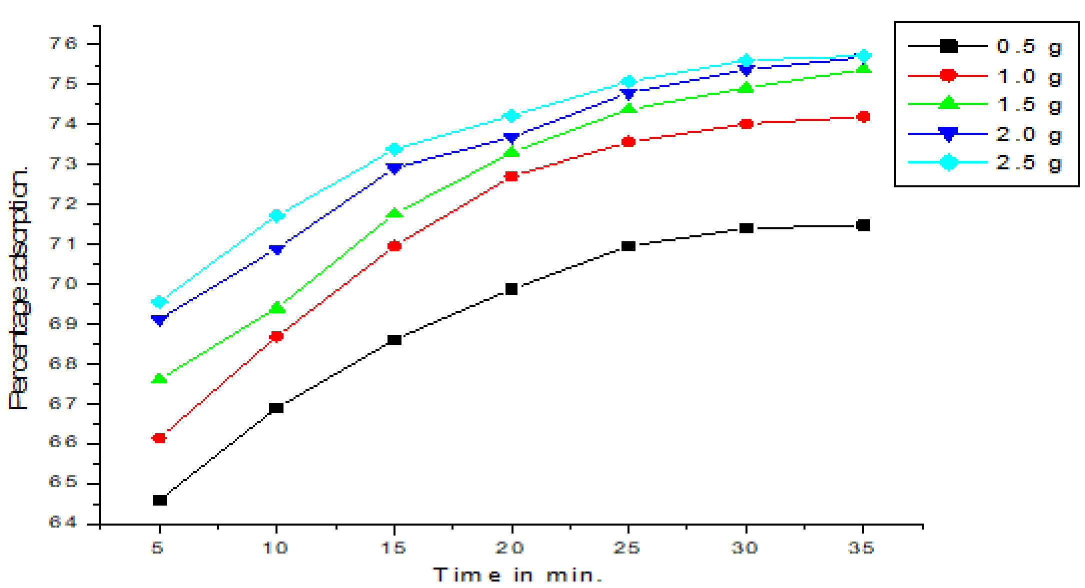

Fig.2: Effect of adsorbent dose of RGSH on adsorpton of MB dye.
[Initial conc.=100 ppm, Volume=50 mL, Temp=298.5k, pH=7]

It has been reported that the adsorption capacity of RGSH for MB increases with increasing adsorbent dosage up to a certain point beyond which the adsorption capacity starts to decrease. This is because at lower doses, fewer adsorption sites are available for MB molecules, resulting in a low adsorption capacity. However, at higher doses, the adsorption sites become saturated and excess adsorbent may even hinder the availability of MB molecules to the active sites, resulting in a decrease in adsorption capacity.

A similar study investigated the adsorption of MB onto red gram peels at different adsorbent dosages (2–10 g/L) [15].

Effect of pH:

The pH of the solution is an important factor that affects the adsorption of MB on the RGSH adsorbent. The surface charge of the adsorbent and the charge of the adsorbate can affect the electrostatic attraction or repulsion between the adsorbent and the adsorbate and thus affect the adsorption process. The effect of solution pH was studied between 2 to 11 as shown in Fig. 3.

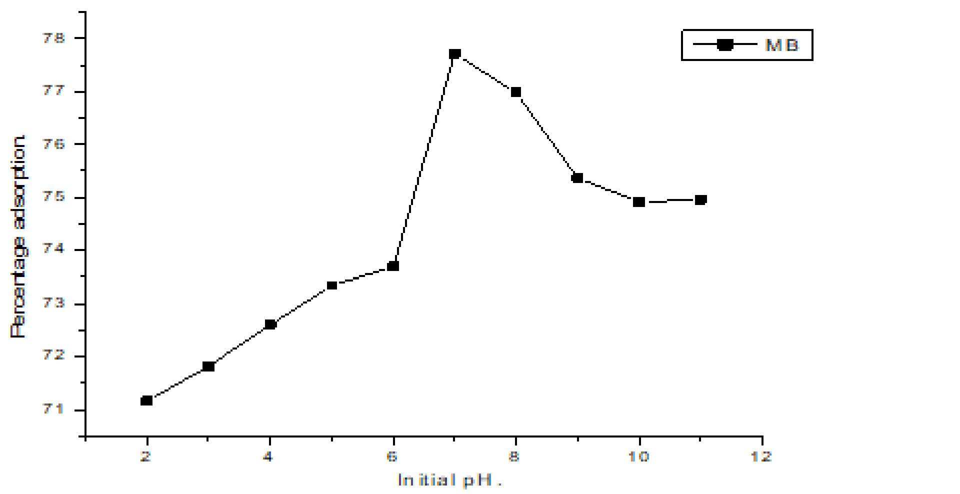

Fig.3:Effect of pH on adsorption of MB dye on RGSH adsorbent.
[Initial conc.=100 ppm, Adsorbent dose=1g, Volume=25mL,Temp=298.5K]

We observed that the adsorption percentage of MB dye increased appreciably with increasing pH from 6-7 and in agreement with the results obtained by others. The adsorption capacity of red gram peels for MB was observed to be pH dependent, with maximum adsorption occurring at a specific pH range.

Effect of temperature:

The adsorption process is affected by temperature due to changes in the surface properties of the adsorbent and the chemical nature of the adsorbate. The temperature effect was investigated for temperatures in the range of 304.8 to 324.8 K. The results are shown in Fig.4.

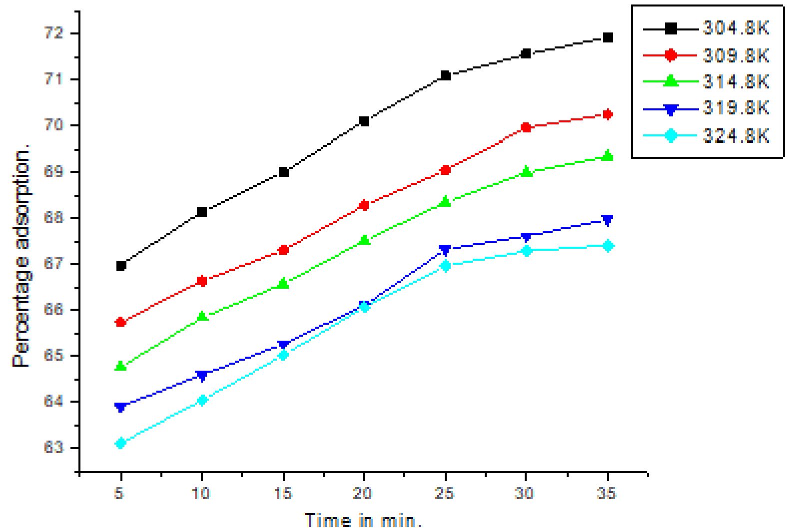

Fig.4:Effect of temperature on adsorption of Mb dye on RGSH adsorbent.
[Adsorbent dose=1.0g, Volume=550 mL, Initial conc.=100ppm, pH=7.0]

The maximum adsorption capacity of MB dye on red gram peel was found to be 67.40 mg/g at 324.8 K, which was a lower capacity than at higher temperatures. Graphical studies report a decrease in the adsorption capacity of RGSH with increasing temperature, suggesting that the process is exothermic and nonspontaneous. Similarly, the maximum adsorption capacity of MB dye on red gram peel was found to be 21.3 mg/g at 25 °C, which was a lower capacity than at higher temperatures [16].

Thermodynamic studies were performed by varying the temperature from 298 to 328 K. The obtained data were used to calculate thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) using the Van't Hoff equation.

$$K_c = \frac{C_{ad}}{C_e} \qquad (3)$$

$$\Delta G^0 = -RT \ln K_c \qquad (4)$$

$$\text{Where,} \quad \Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (5)$$

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \qquad (6)$$

Where K_c is the equilibrium constant, C_{ad} is the concentration of MB solution adsorbed per liter of solution at equilibrium, C_e is the equilibrium concentration (mg/L) of MB in solution, T is the temperature in Kelvin and R is the gas constant (8.314 J/mol). The values of ΔH^0 and ΔS^0, were determined from the slopes and intercepts of the plot of $\log K_c$ versus $\frac{1}{T}$, respectively.

Table 1: Thermodynamic parameter values of RGSH adsorbent with MB solution at different temperatures.

Temperature (K)	(ΔG°) KJ/mole	(ΔH°) KJ/mole	(ΔS°) J/mole
304.8	- 3.238163497	- 16.389	- 43.146
309.8	- 3.022434567		
314.8	- 2.806705637		
319.8	- 2.590976707		
324.8	- 2.375247777		

The ΔG^0 values obtained in this study for MB dye are <-10 KJ/mol indicates that physical adsorption was the predominant mechanism in the adsorption process. Gibb's free energy indicates the degree of spontaneity of the adsorption process, where a more negative value reflects a more energetically favorable adsorption process. A negative value of ΔG^0(Table:1.) shows that the adsorption is favorable and spontaneous [17,18]. The negative value of ΔS^0 and ΔH^0 indicates that the reduced disorder and randomness at the solid solution interface with exothermic adsorption.

Adsorption isotherm:

An adsorption isotherm is a graphical representation of the equilibrium relationship between the concentration of adsorbate (in this case MB dye) in solution and the amount of adsorbent (red gram seed husk) required for adsorption at constant temperature. The most commonly used adsorption isotherm models are the Langmuir and Freundlich isotherm models.

Langmuir isotherm:

The Langmuir adsorption isotherm quantitatively describes the formation of a monolayer adsorbate on the outer surface of the adsorbent, after which no further adsorption takes place. The Langmuir isotherm applies to the adsorption of a monolayer onto a surface containing a finite number of identical sites. The linear form of the equation is given by

$$\frac{1}{q_e} = \left(\frac{1}{Q_0}\right) + \frac{1}{bQ_0C_e} \qquad (7)$$

Where C_e (mg/L) is the equilibrium adsorbate concentration, q_e (mg/gm) is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium, Q_0 (mg/gm) and b (L/mg) are the Langmuir constants relating to the maximum adsorption capacity of the monolayer and the energy of adsorption. 'Q_0'' and 'b' are calculated from the slope and intercept of the $\frac{1}{q_e}$ versus $\frac{1}{C_e}$1 plot, respectively. The basic features of the Langmuir isotherm can be expressed using the equilibrium parameter R_L. Which is a dimensionless constant referred to as the separation factor or equilibrium parameter [19].

$$R_L = \frac{1}{1+bC_0} \quad (8)$$

Where C_0 the initial concentration in ppm and b is the Langmuir constant related to energy adsorption. The value of R_L indicates the nature of adsorption as either unfavorable if $R_L > 1$, linear, if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$ [20].

Freundlich isotherm:

Freundlich presented an empirical adsorption isotherm for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is also expressed as

$$\frac{x}{m} = K_f C_e^{1/n} \quad (9)$$

Where x is the amount adsorbed, m is the mass of adsorbent, C_e is the equilibrium concentration of adsorbate (mg/L), The constants K_f and n can be obtained by taking the *log* of both sides of equation (9) as follows,

$$\log\frac{x}{m} = \frac{1}{n}\log C_e + \log K_f \quad (10)$$

The constant K_f is an approximate indicator of the adsorption capacity, while $\frac{1}{n}$ is a function of the adsorption strength in the adsorption process [21]. If $n = 1$, then the partitioning between the two phases is independent of concentration. If the value of $\frac{1}{n}$ is lower than one, it means normal adsorption, on the other hand, the value of $\frac{1}{n}$ higher than one means cooperative adsorption [22]. A plot of $\log\frac{x}{m}$ against $\log C_e$ gives a straight line with the intercept on the ordinate axis. The value of n and K_f can be obtained from the slope and intercept of the linear graph.

Table 2: Isotherm parameter values of RGSH with MB dye solution.

Concentration of MB dye solution *(ppm)*	*Langmuir constants*				*Freundlich constants*		
	Q_0 *(mg/gm.)*	$b*10^{-3}$ *(L/gm.)*	R_L	R^2	n	K_f*(mg/gm.(L/gm.))*$^{1/n}$	R^2
20	357.83	0.020	0.998	0.999	1.210	17.3972	0.998

The $\boldsymbol{R_L}$ value was found to be between *0* and *1* for the MB dye solution. It is confirmed that the continued adsorption of the MB dye solution is favorable. The data show that both the Langmuir model and the Freundlich model provide a better fit. The value of n indicates that the deviation from linearity, if $n = 1$, the adsorption is homogeneous and there is no interaction between the adsorbed species. The value of n is greater than one, ($1 < n < 10$), which means favorable adsorption [23]. If the value of $\frac{1}{n} > 1$ means that adsorption is favored and new adsorption sites are generated [24-27]. The value of *n* shown in the table: 2. The value of *n* was found to be between *1* and *10*, indicating favorable adsorption.

***Adsorption kinetics*:**

Adsorption kinetics is the study of the rate at which adsorbate (in this case MB dye) is adsorbed onto an adsorbent (red gram seed husk). The most commonly used models to describe the adsorption kinetics of MB dye on the skin of red gram seed are pseudo-first and pseudo-second order models.

The pseudo-first-order model assumes that the rate of adsorption is proportional to the difference between the equilibrium adsorption capacity and the amount of adsorbate adsorbed in a given time. The model can be expressed by the following equation:

$$\frac{dq}{dt} = K_1(q_e - q_t) \quad (11)$$

After some integration by applying the $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$ equation (11) becomes,

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (12)$$

Where, q_e(mg/gm) is the amount of adsorption at equilibrium, q_t (mg/gm) indicates the amount of adsorption at time t (min), and K_1(min^{-1}) is the rate constant of the pseudo first-ordermodel. Based on the experimental results, linear plots were plotted between $\log(q_e - q_t)$ versus t, to calculate K_1, q_e and R^2.

The pseudo-second-order model, on the other hand, assumes that the rate of adsorption is proportional to the square of the amount of adsorbate adsorbed in a given time. The model can be expressed by the following equation:

A pseudo-second order equation is developed Ho can be written as

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \quad (13)$$

Where, K_2 *(gm.mg^{-1}min^{-1})* is the pseudo-second order rate constant. By integrating equation (13) for boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$ the linear form of the equation is

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \quad (14)$$

K_2 and q_e can be obtained from the intercept and slope of a plot of $\frac{t}{q_t}$ against t.

Table 3: Kinetic parameter values of RGSH with MB dye solution

Concentration of MB dye solution (ppm)	*Pseudo-First order*			*Pseudo-first order*		
	K_1 *(min^{-1})*	q_e *(mg/gm)*	R^2	K_2 *(gm/mg. min)*	q_e *(mg/gm)*	R^2
20	$3.636*10^{-2}$	616.31	0.882	$3.21*10^{-2}$	3839.39	0.999

The R^2 value with first order kinetics was 0.998, while for second order it is 0.999 for RGSH adsorbent. It is clear that the adsorption of the MB dye solution on the RGSH adsorbent was better represented by pseudo second order kinetics. This indicates that the adsorption system belongs to the second-order kinetic model.

4. Conclusion

The study of the kinetics, equilibrium and thermodynamics of methylene blue (MB) adsorption onto red gram seed husk as bio-adsorbent provided valuable insights into the behavior of the adsorption process. The pseudo-second-order model was found to fit the experimental data better than the pseudo-first-order model, suggesting that the rate-limiting step in the adsorption process is the chemical reaction between MB and the active sites on the bio-adsorbent. The Langmuir isotherm was found to be the most appropriate adsorption isotherm to describe the adsorption behavior, indicating that adsorption occurs at specific homogeneous sites on the adsorbent surface. Thermodynamic studies have shown that the adsorption process is spontaneous, exothermic and accompanied by an increase in disorder or randomness.

Overall, the results of this study suggest that red gram seed husk can be an effective bio-adsorbent for the removal of MB from aqueous solutions. This research can be helpful in the development of wastewater treatment systems for industries that use MB and other similar dyes, thereby reducing the environmental and health risks associated with their release into the environment.

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