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SEM of *Theobroma cacao*

Kinetics and Thermodynamics of Sorption of Methylene Blue Dye Onto Raw Groundnut Shell Biosorbent

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ABSTRACT

Dyes are one of the hazardous chemicals found in wastewater produced by textile and allied industries that need to be removed from the wastewater before it is released into water bodies. The sorption efficiency of raw groundnut shell (RGS), an agricultural waste, was tested on methylene blue (MB) dye through a batch adsorption experiment. Physicochemical analysis of the RGS indicated good biosorbent properties. Fourier transform infrared (FTIR) spectroscopy analysis of the RGS revealed the presence of heterofunctional groups. The effect of various biosorption parameters such as initial dye concentration, contact time, and biosorbent dosage wAS systematically investigated. The quantity of MB adsorbed increased as the initial concentration and contact time increased and decreased with an increase in biosorbent dose. A maximum uptake capacity of 29.3 mg/g was recorded for 50 mg/L MB initial concentration. The equilibrium data from the batch adsorption experiments were fitted well into Freundlich isotherm and pseudo-second-order kinetic models. The results from this study indicate that RGS can serve as an alternative, low-cost, eco-friendly and efficient adsorbent for the removal of MB dye from wastewater.

INTRODUCTION

A safer and cleaner environment is one of the most important requirements of all living organisms on earth, including humans [1]. Wastewater from textile and related industries creates serious problems for the environment if discharged without adequate treatment causing water pollution because of the coloring agents from residues of dyes and various chemical additives which are toxic and harmful to living organisms [2,3].

Methylene blue (MB) chemically known as methylthioninium chloride ($C_{16}H_{18}ClN_3S$) is a synthetic cationic dye with a thiazine structure, it has wide applications in pharmaceutical, textile, personal care, food, and printing industries [4]. However, MB has some health effects on human beings such as headache, shortness of breath, vomiting, cause excessive sweating if inhaled through water, permanent eye damage for prolonged exposure, and methemoglobinemia-like syndromes [4–6]. Therefore, MB must be removed from industrial effluents before it is discharged into the eco-system. Several physicochemical techniques have been explored for the removal of MB and other contaminants in aqueous solution, this includes coagulation, ion exchange, precipitation, flocculation, nano-membrane filtration, ozonation, and adsorption [3,6]. Most of the techniques mentioned are not efficient and difficult to scale up and as such are not economically viable [7]. However, adsorption is considered one of the most efficient techniques because of its several advantages which include flexibility in operations and design, cost-effectiveness, reusability of adsorbents, reliability, and a high capacity of decontamination [1,6].

Activated carbon has been a conventional adsorbent used for wastewater treatment because of its high porosity and surface area. However, activated carbon as an adsorbent has some disadvantages such as the high cost of production, and regeneration, especially in large-scale applications, and is not readily available [8]. To overcome these drawbacks, different agriculture-based waste products have been explored by researchers as an alternative low-cost adsorbent such as black tea

wastes [5], groundnut and sorghum husks [9,10], *Archidendron jiringa* seed shells [11], rice husk [12,13], coconut shells [14], *Balanites aegyptiaca* seed husks [15], walnut shell [16], nance (*Byrsonima crassifolia*) seeds and peels [4] and sugarcane bagasse and wheat bran [6].

Groundnut shell (GS) is an agricultural waste from groundnut processing which is cultivated in many countries around the world with China, India, Nigeria, Senegal and Sudan as main producers and it contains cellulose, lignin and other fibrous carbonaceous materials [17,18]. It constitutes part of solid waste disposal problem generally encountered in most of the developing countries where it is cultivated [17,19]. Therefore, it is of great interest to use GS as an alternative adsorbent due to its natural abundance, non-toxic nature, and low commercial value [18]. At the same time, this will greatly help in solving the solid waste disposal problem of the groundnut oil industry.

Thus, in this study, the raw groundnut shell (RGS) without any chemical treatment was utilized for the adsorption of the MB dye from the aqueous solution. The effectiveness of its adsorption capacity was systematically studied through equilibrium, kinetics, and thermodynamics of the biosorption experiment.

MATERIALS AND METHODS

Sample collection and preparation

Groundnut shells (GS) were collected from Zambuk in the Yamaltu-Deba local government area of Gombe State (10º 14' 17" N, 11º 26' 30" E of Greenwich meridian). The sample was initially washed with tap water followed by distilled water, dried in an oven at 50 ºC for 24 h, and then crushed into powder with a grinder. The powder materials were then sieved with a standard sieve to obtain particles within the size range of (200-250) µm and were kept in an air-tight plastic container. For the purification of the GS samples, 100 g was contacted with distilled water at room temperature for 24 h. It was filtered and air-dried for 8 hours [10,20].

Preparation of Methylene Blue solutions

A 1000 mg/L stock solution of MB dye was prepared by weighing 1.0 g of MB and dissolved into 1000 mL of deionized water. 5-60 mg/L working concentrations were prepared by serial dilution.

Surface characterization of biosorbent

Fourier transform infrared (FTIR) analysis of the RGS was recorded using FTIR model 8400s in the range of 400 cm^{-1} and 4000 cm^{-1} to obtain the functional groups present in the RGS sample.

Physicochemical characterization of biosorbent

Determination of pH

A 5 g of biosorbent sample was dissolved in 100 mL of deionized water. The mixture was heated to 100 ºC and kept at that temperature for 15 minutes after which it was allowed to cool to 70 ºC and filtered. The filtrate was allowed to cool to room temperature. The pH of the filtrate was measured and recorded using a digital pH meter [21].

Determination of bulk density

A cleaned and dried measuring cylinder with 10 mL capacity was weighed and recorded as W_0. it was filled to the 10 mL mark with the biosorbent sample. the measuring cylinder containing the sample was tapped for 200 counts, thereby compacting the sample so that the volume of the sample now dropped to a mark V mL. This was then weighed and recorded as W_2. The weight of the sample in grams divided by the final volume V, which represents the bulk density in g/mL of the biosorbent was calculated using the expression [22]:

Bulk density = $(W_2 - W_0) / V$.

Determination of ash content

A 2 g sample of the biosorbent was weighed into an empty clean crucible that had been previously ignited, cooled, and weighed. This was then kept in the furnace at 600 °C for 5 h and then allowed to cool to about 200 °C. The crucible was transferred directly into a desiccator to cool to room temperature and weighed immediately. The percentage (%) ash content was calculated as follows [22]:

$$\frac{(\text{mass of crucible} + \text{ash}) - (\text{mass of empty crucible})}{\text{mass of sample}} \times 100$$

Determination of moisture content

A clean crucible was dried in an oven at 103 ºC for 1 h, cooled in a desiccator, and the mass of the crucible was recorded as W_o. A 5 g sample of the biosorbent was placed inside the clean and previously weighed crucible. The crucible was placed in an oven at 103 ºC for 2 h, cooled in a desiccator, and weighed. The same procedure was conducted severally until a constant concomitant mass was obtained. The decrease in mass represents the moisture content of the sample and this was calculated thus [21]:

$$\%\ Moisture\ Content = \frac{X-Y}{X-W_o} \times 100$$

where the mass of the empty crucible = W_o; the mass of the sample and crucible before drying = X and the mass of the sample and crucible after drying = Y.

Determination of crude fiber content

A 1 g sample of the biosorbent was weighed into a standard flask, 150 mL of 0.128 M sulfuric acid solution, and 3 drops of an anti-foaming agent were added into the flask. The mixture was refluxed for 30 minutes. It was filtered, washed with hot deionized water, and dried (denoted A). The same procedure was repeated using 0.223 M NaOH. finally, the sample was ashed at 550 ºC for 5 h, cooled to room temperature, and weighed (denoted B) [22]. The % crude fiber content is given as:

$$\frac{Mass\ of sample\ in\ A - Mass\ of sample\ in\ B}{1} \times 100$$

Determination of surface area

A 0.5 g sample of the biosorbent was added to 0.1 M HCl. The pH of the mixture was adjusted to 3-3.5 after the addition of 10 g NaCl. The mixture was diluted to 50 mL with distilled water. The mixture was titrated against standard 0.1 M NaOH until pH 4 and then to pH 9. The volume of NaOH required to raise the pH from 4 to 9 was recorded. The surface area of the biosorbent was estimated from the equation below [21]:

$$S = 32V - 25.$$

where S is the surface area (m^2/g) and V is the volume (mL) of NaOH required to raise the pH.

Determination of iodine number

A blank titration was conducted using 10 mL of 0.1 N iodine solution with a starch solution as an indicator. The solution was titrated against 0.05 N sodium thiosulphate and the titer value was recorded as B. 40 mL of 0.1 N iodine solution was added to 0.2 g of the biosorbent in a container, and the mixture was stirred vigorously and filtered. 10 mL of the filtrate was pipetted and titrated against standard sodium thiosulphate solution using starch as an indicator and the titer value was recorded as A [22]. The iodine number was calculated as follows:

Iodine number = C x CF (CF is the conversion factor).

$$\text{CF} = \text{Mw of iodine x } \frac{40}{\text{mass of sample}} \text{ x blank reading}$$

and C = B-A.

Batch adsorption experiment

A batch biosorption experiment was used for the adsorption of MB from aqueous solution using the raw groundnut shell (RGS). This was conducted through process optimization of different parameters such as contact time, biosorbent dose, initial dye concentration, and temperature. 50 mL of different MB concentrations (10-100 mg/l) was contacted with 0.1 g of the RGS and placed in an orbital shaker for 2 h. The solutions were filtered quickly at the end of this period and the filtrates were subjected to UV-Visible spectrophotometer analysis at 665 nm to obtain the remaining concentration of the dye solution. The uptake capacity of the biosorbent (Q, mg/g) was calculated using equation 1:

$$Q = \frac{V(C_o - C_f)}{m} \qquad (1)$$

where C_o and C_f are the initial and final concentration (mg/L) of dye solution, V (L) is the volume of the dye solution and m is the mass of biosorbent (g) [23]. Other equilibrium parameters such as contact time (10-150 minutes), biosorbent dose (0.1-0.5 g), and temperature (30-50 ºC) were optimized following the same procedure. The original pH of all the solutions was used without any adjustment. The data obtained from the biosorption experiments were tested with Langmuir and Freundlich isotherms using equations 2 and 3 respectively [16]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_o b} + \frac{1}{Q_O} C_e \qquad (2)$$

$$\log q_e = \log K_f + (1/n) \log C_e \qquad (3)$$

where Ce (mg/L) is the concentration of the dye at equilibrium, Q_e (mg/g) is the quantity adsorbed per unit mass, Q_0 and b are constants related to Langmuir adsorption capacity and rate of adsorption respectively. If the plot of (C_e/Q_e) against C_e is linear, it indicates that the adsorption fitted into the Langmuir model. The constants Q_0 and b can be deduced from the slope and intercept of the plot. K_f (mg/g) indicates adsorption capacity and 1/n is the adsorption intensity. The values of K_f and n are determined from the intercept and slope of the linear plot of log q_e against log C_e.

Biosorption kinetics and thermodynamics

The biosorption kinetics of the MB by RGS were subjected to pseudo-first-order and pseudo-second-order kinetic models as expressed by equation 4 and 5 respectively [10]:

$$log(q_e - q_t) = log\, q_e - \frac{k_{s1}}{2.303} t \qquad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_{s2} {q_e}^2} + \frac{t}{q_e} \qquad (5)$$

where q_e and q_t (mg/g) represent quantities adsorbed at equilibrium and at time t, respectively, k_{s1} (min^{-1}) and k_{s2} (g/mg.min) represent pseudo-first-order and second-order rate constants respectively. A linear plot of log $(q_e - q_t)$ and t/q_t against t indicates the experimental data fitted into pseudo-first-order and second-order respectively. The values of k_{s1}, k_{s2}, and q_e can be obtained from the slope and intercept of the graph. Gibbs free energy change, ΔG, change in entropy, ΔS, and change in enthalpy, ΔH as thermodynamic quantities were evaluated from equations 6 and 7 [24,25]:

$$Ln\, k_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (6)$$

$$\Delta G^\circ_{ads} = \Delta H^\circ_{ads} - T\Delta S^\circ_{ads} \qquad (7)$$

where k_d represents the adsorption distribution coefficient and T is the absolute temperature (K).

RESULTS AND DISCUSSION

The physicochemical properties of biosorbents are one of their essential features and they are indicative of their potential for environmental bioremediation. The results obtained for RGS are summarized in **Table** 1. pH of a biosorbent gives a degree of acidity or alkalinity of the biosorbent. From **Table** 1, it can be observed that the pH of the RGS biosorbent had a slightly alkaline value of 7.8, This is due to the presence of minerals such as sodium and potassium (as constituents of ash) in the biosorbent. These minerals give a basic solution upon dissociation in water which is responsible for the alkaline pH of RGS. This is in agreement with the relatively low ash contents of 11.5 % recorded for the biosorbent.

It has been suggested that for most applications of biosorbents (like wastewater treatment), pH values of 6.0 – 8.0 and low ash contents are desirable features for biosorbents [18,26]. This will prevent the blocking of existing pores in the biosorbents active site and therefore give a larger surface area and higher carbon content [7,10]. This is further collaborated by higher crude fibre content of 52.3 % which is a measure of the cellulose and lignin contents in the biosorbent. The lower moisture content of 6.2 % and a bulk density of 0.34 g/mL were determined for the biosorbent, lower moisture content indicates that the biosorbent can be stored for a longer period without being contaminated by microorganisms. These values fall within the range of many biosorbents reported in the literature [2,17,27]. Surface area and iodine number are the most fundamental parameters used to characterize biosorbent performance [22]. A high surface area of 35.8 m^2/g was estimated for the biosorbent. This value is greater than the 3.85 m^2/g BET surface reported for GS by other studies [17]. Similarly, a high iodine number of 881.1 mg/g was also estimated for the biosorbent.

Table 1. Physicochemical properties of RGS biosorbent

Property	Value
pH	7.8
Ash content (%)	11.5
Crude fiber (%)	52.3
Moisture content (%)	6.2
Bulk density (g/mL)	0.34
Iodine number (mg/g)	881.1
Surface area (m^2/g)	35.8

FTIR spectroscopy of RGS biosorbent

The FTIR spectra obtained for the RGS biosorbent recorded within the spectral range of 4000-450 cm^{-1} is shown in **Fig. 1**. A broad absorption band at 3427 cm^{-1} observed correspond to O-H vibration, 2922 cm^{-1} correspond to C-H stretching, 1631 cm^{-1} correspond to carbonyl group, C=O and 1422 cm^{-1} can be assigned to aromatic C=C, these are indicative of alkenes and aromatic functional groups in the biosorbent. The presence of these functional groups on the surface of the biosorbent is likely to facilitate contact between the biosorbent and the MB dye which will increase the biosorption capacity.

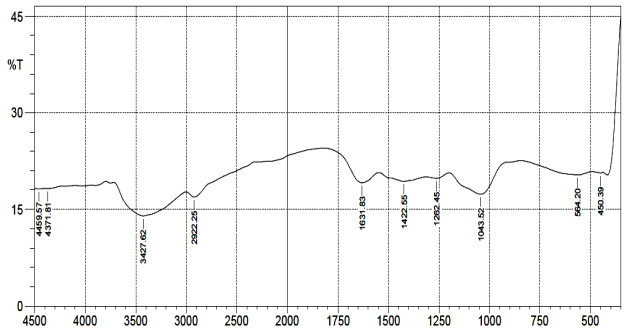

Fig. 1. FTIR spectrum of RGS biosorbent

Effect of initial dye concentration

The effect of initial dye concentration was studied in the concentration range of 5-60 mg/L. the quantity of MB dye adsorbed at the various concentrations was depicted in **Fig. 2**. It can be observed that there is a progressive increase in the quantity of MB adsorbed as the initial concentration increased due to the driving force that exists between the MB solution and the biosorbent to overcome the mass transfer resistance of the dye solution [10]. It can be seen from **Fig. 2** that as the concentration of MB dye increases to 50 mg/L the quantity adsorbed (Q) also increases to 29.3 mg/g. Further, an increase in a concentration above 50 mg/L leads to a decrease in the quantity adsorbed, this indicates that an equilibrium concentration has been reached at this initial concentration.

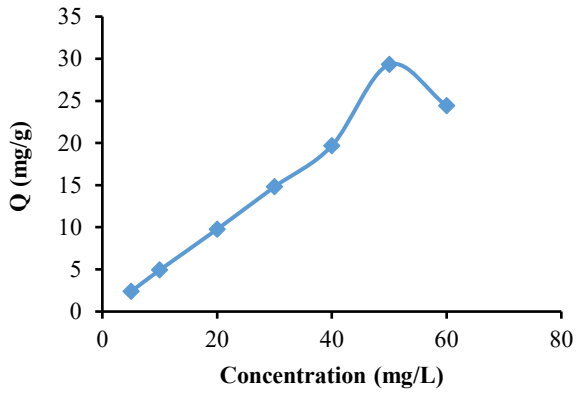

Fig. 2. Effect of initial dye concentration on MB biosorption by RGS.

Effect of contact time

The effect of the contact time of biosorbent with adsorbate plays a significant role in the adsorption process by greatly influencing the adsorption capacity. The effect of contact time was studied for the time interval of 10-150 min as shown in **Fig. 3**. From 10-20 min of contact time, there is no significant increase in quantity adsorbed. This may be due to insufficient agitation time. As agitation time is increased from 20 to 90 min there was a progressive increase in dye adsorption from about 22 to 25 mg/g which may be attributed to reduced diffusion layer thickness surrounding the biosorbent particles [2]. Increasing contact time from 90 to 150 min leads to a gradual decrease in sorption capacity which indicates that equilibrium was attained. The maximum quantity of 25 mg/g was adsorbed at an equilibrium time of 90 min.

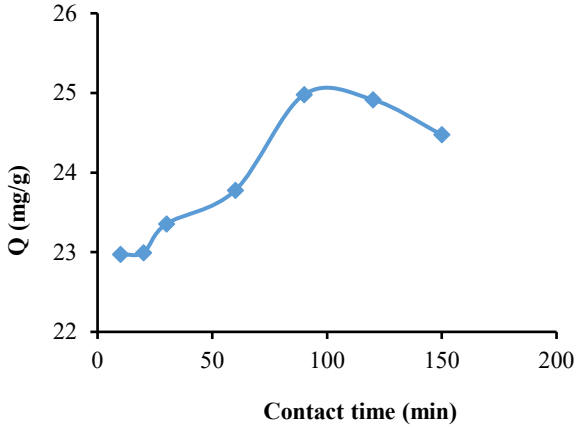

Fig. 3. Effect of contact time on MB biosorption by RGS.

Effect of biosorbent dosage

The biosorbent dose is another important parameter in the adsorption process because it influences the capacity of biosorbent for a given initial concentration of dye solution. It can be observed in **Fig. 4** that the quantity adsorbed decreased continuously with an increase in biosorbent mass which is in the range of 0.1-0.5 g. This may be attributed to the aggregation/agglomeration of biosorbent particles at higher doses, leading to the saturation of the surface area, an increase in the diffusional path length, and the attainment of equilibrium [27]. The maximum quantity adsorbed was achieved using 0.1 g mass of the biosorbent.

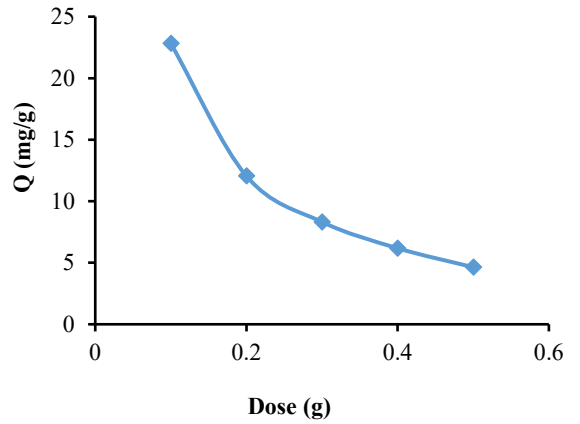

Fig. 4. Effect of biosorbent dose on MB biosorption by RGS.

Effect of temperature

Normally temperature stimulates the mobility of molecules and ions in the solution and thereby affecting the surface morphology of the biosorbent during the adsorption processes [9]. The effect of temperature on the quantity of MB dye adsorbed by RGS was studied at the temperature range of 30-50 °C as shown in **Fig. 5**. The quantity adsorbed increases rapidly as the temperature is

increased from 30 to 40 °C and remains constant as the temperature is increased to 50 °C. The initial increase in quantity adsorbed may be attributed to the reduced viscosity of the solution and increased mobility of dye molecules leading to rapid contact between the biosorbent and the dye molecules. Meanwhile, the decrease in quantity adsorbed at 50 °C may be due to the desorption of dye molecules from the surface of the biosorbent [9].

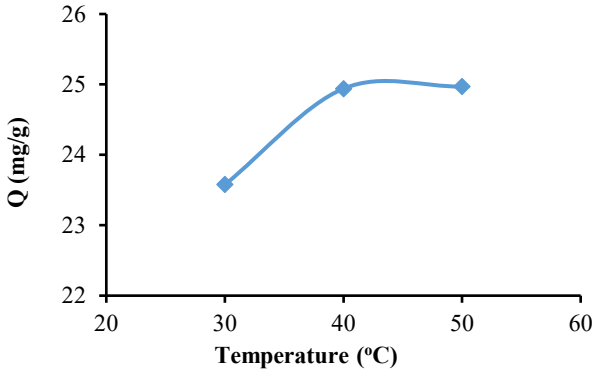

Fig. 5. Effect of temperature on MB biosorption by RGS.

Biosorption isotherm studies

Adsorption isotherms are important models to describe how the adsorbate interacts with the biosorbent at the solid-solution interface and is critical in determining the optimum quantity adsorbed at equilibrium [10,20]. The equilibrium experimental data obtained in this study was fitted with two isotherms models namely; Langmuir and Freundlich isotherms. The Langmuir plot is depicted in **Fig. 6** and the parameters obtained from the plot are summarized in **Table 2**.

The value of 0.387 L/mg was obtained for the constant b, which is related to the energy of adsorption. comparatively, this is higher than the reported values of 0.037 [27], 0.0245 [19], and 0.011 [24]. The constant Q_o indicates Langmuir adsorption capacity, it was calculated from the plot to be 11.28 mg/g. This is higher than most of the reported values for MB adsorption using groundnut shell biosorbent which is in the range of 4.21-7.052 mg/g [10,18,28].

The Freundlich plot for the sorption system studied is given in **Fig. 7** and the corresponding constants are summarized in **Table 2**. The constant n, indicates the intensity of adsorption and the nature of the biosorbent's surface in a dilute solution. Values greater than 0 but lower than 1 indicate a less heterogeneous surface of the biosorbent while K_f value indicates the adsorption capacity between adsorbate and biosorbent [4]. Both Langmuir and Freundlich models show good correlation coefficients ($R^2 >$ 0.97).

Table 2. Equilibrium isotherms parameters

Langmuir			Freundlich		
Q_o(mg/g)	b (L/mg)	R^2	K_f(mg/g)	n	R^2
11.28	0.387	0.9706	5.41	0.72	0.9809

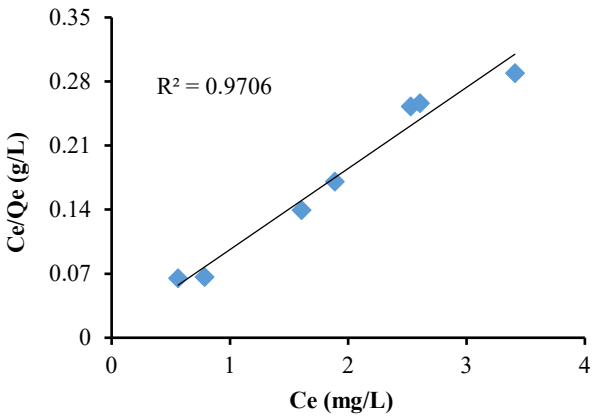

Fig. 6. Langmuir isotherm plot for the biosorption of MB onto RGS.

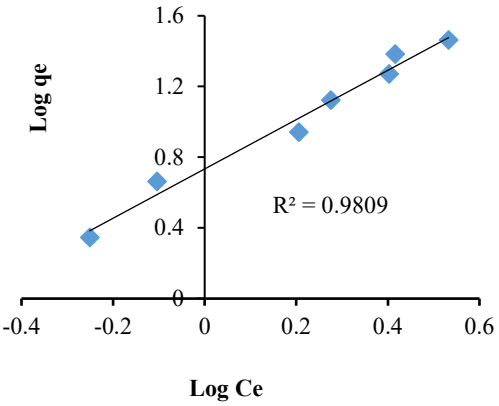

Fig. 7. Freundlich isotherm plot for the biosorption of MB onto RGS.

Biosorption kinetics

The kinetic study is an essential factor that determines the efficiency of biosorption processes. It is used to investigate adsorption mechanisms and adsorption characteristics [11]. In this study, the experimental data were analyzed using pseudo-first-order and pseudo-second-order kinetic models. Using equations 4 and 5, pseudo-first-order and second-order plots were obtained and are depicted in **Fig. 8** and **9** respectively. The constant values from these plots are given in **Table 3**. From this table, it can be seen that the correlation coefficients, R^2 from both models show good linearity with the pseudo-second-order model showing higher R^2 (0.9988) indicating that the adsorption of MB by RGS is best described by the pseudo-second-order kinetics. Hence the biosorption process is said to be controlled by chemisorption and This suggests that the film diffusion on the external surface of the biosorbent is the rate-determining step [10].

Table 3. Kinetic models parameters for MB biosorption onto RGS

Pseudo first order			Pseudo second order		
K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/mg/min)	q_e(mg/g)	R^2
0.0092	2.23	0.9706	2.07	2.52	0.9988

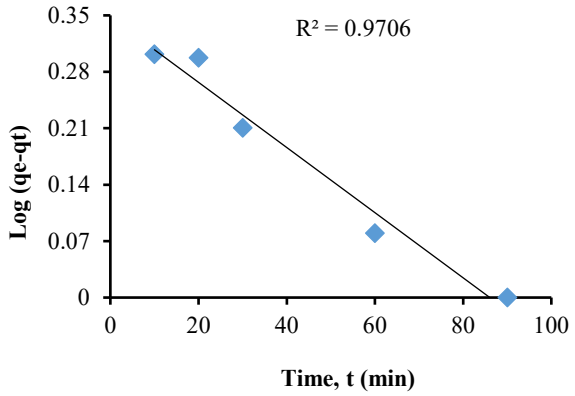

Fig 8. Pseudo-first order plot for biosorption of MB onto RGS.

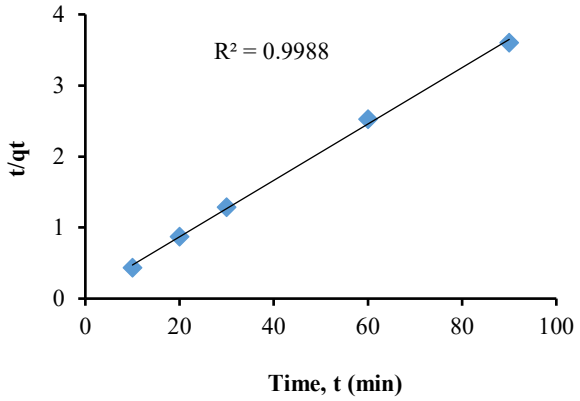

Fig 9. Pseudo-second order plot for biosorption of MB onto RGS.

Biosorption thermodynamics

Thermodynamic parameters can be useful in the evaluation of the orientation of the physicochemical biosorption reaction. It provides useful information regarding the inherent energy, structural changes, and the mechanism involved in the adsorption process. The thermodynamic parameters of the biosorption process were evaluated using equations 6 and 7 at 303, 313, and 323 K as presented in **Table 4**. A plot of ln K against 1/T gives a good correlation coefficient, R^2 of 0.9674 as shown in **Fig. 10**. The values of ΔG°_{ads} are all negative and increased slightly with an increase in temperature, this indicates enhanced biosorption of MB at moderate temperature and a spontaneous process. However, the positive values of ΔH°_{ads} and ΔS°_{ads} obtained indicated physisorption, an endothermic process, and increased randomness of the solid−solution interface for the MB biosorption process [16,24,25].

Table 4. Thermodynamic parameters of MB dye biosorption onto RGS.

Temperature (K)	ΔG°_{ads} (kJ/mol)	ΔH°_{ads} (kJ/mol)	ΔS°_{ads} (J/mol k)
303	-40.41		
313	-41.75	30.82	133.48
323	-43.08		

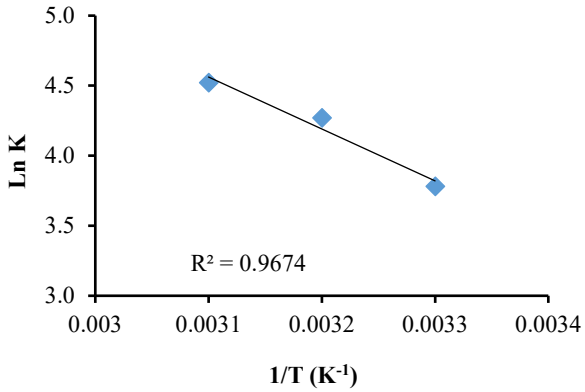

Fig. 10. Thermodynamics plot for MB dye biosorption onto RGS.

CONCLUSION

In this study, raw groundnut shell (RGS) was utilized as biosorbent for the adsorption of MB from an aqueous solution. A batch biosorption study was employed for the removal of the MB through process optimization of contact time, initial concentration, biosorbent dosage, and temperature. A maximum uptake capacity of 29.3 mg/g was achieved at equilibrium. The biosorption kinetics and isotherms analysis showed that the removal of the MB by RGS conformed to the pseudo-second-order and the Freundlich models. Furthermore, the thermodynamic study indicates that the biosorption of the MB is a spontaneous, an endothermic, and physisorption process. Based on these findings, it can be concluded that the RGS as a low-cost, and eco-friendly biosorbent is highly efficient in MB removal from wastewater.

CONFLICT OF INTEREST

The authors declared that there is no conflict of interest.

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