

Adsorption Isotherm of Methylene Blue Dye on Groundnut Shell and Sorghum Husk

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ABSTRACT

Dye removal using low cost adsorbent is a suitable method for textile wastewater treatment. The aim of this research work is application of groundnut shell and sorghum husk in powdered form as low cost adsorbent for methylene blue and Congo red dye removal from water at laboratory scale. Batch studies were carried out to determine the adsorption equilibrium of methylene blue and Congo red dye on the two different adsorbent and also to verify the reported data using Langmuir, Freundlich and Temkin isotherm. The study revealed that for the adsorption of methylene blue on sorghum husk, Langmuir Isotherm fitted well the experimental data with R^2 value of 0.9710, while for the adsorption of methylene blue on groundnut shell. The Temkin binding energy (b_T) are positive for all the experiment, indicating that the process is endothermic. The present work will help to carry out studies in packed column and later scale it up for industrial application.

Keywords: Temkin binding energy; Dyes; Langmuir constant; Adsorption isotherm; Sorbet

Abbreviation: MB: Methylene Blue dye; GS: Groundnut Shell; SH: Sorghum Husk; UV: Ultraviolet spectrophotometer

INTRODUCTION

The released voluminous amount of toxic substances in to the water system has affected the human beings as well as aquatic animals. Dyes are used extensively in various industries such as textiles rubbers plasticss printings leathers cosmeticss etc., and also in production of colored products. Dyes affect the penetration of sunlight into the water bodies and thus interfere with the growth of bacteria and hinder photosynthesis in aquatic plant. It poses a serious threat to mankind and water qualitys thereby is a matter of vital concern. It causes acute and chronic effects on exposure to human skins such as allergics dermatitiss skin irritations cancers mutation etc. It is very difficult to separate dye from water by using conventional techniques [1]. Among the various treatment methods adsorption process chemical coagulation flocculation degradation process etc. have been explored to remediate these dyes in the waste water [2]. Among the various techniques available for its remediation adsorption technique has been proved to be most efective process. Adsorption is preferred over other processes due to possible regeneration and recovery of the sorbet.

Adsorption is a unit operation process which refers to attachment of molecules of liquid or gas on the surface solid substance. It is based on the fact that some solids preferentially adsorb other solute from the solution onto their surfaces. Dyes are particularly removed using various adsorbents. Many such adsorbents have been explored for its removal. However in this research work we considered adsorption process using groundnut shell and sorghum husk.

Problem statement

The world is becoming more industrialized therefore the amount of toxic material (e.g. dye) released in to the environment is becoming highs some agricultural by-product can be used for water purification so as to comply with the environmental regulation.

Aim and objective

The aim of the research work is to study the adsorption isotherm for methylene blue dye on groundnut shell and sorghum husk.

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Received: 11-Mar-2024, Manuscript No. JCEPT-24-30096; **Editor assigned:** 14-Mar-2024, PreQC No. JCEPT-24-30096 (PQ); **Reviewed:** 28-Mar-2024, QC No. JCEPT-24-30096; **Revised:** 04-Mar-2025, Manuscript No. JCEPT-24-30096 (R); **Published:** 11-Mar-2025, DOI: 10.35248/2157-7048.25.16.524

Citation: Sunday K, Amarachi EI (2025) Adsorption Isotherm of Methylene Blue Dye on Groundnut Shell and Sorghum Husk. J Chem Eng Process Technol. 16:524.

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The objectives of the research work are:

- To determine the adsorption isotherm that best fits the batch adsorption data.
- To determine values of Langmuir's Freundlich and Temkin constants which defined the adsorption process.

Scope

The research is limited to the adsorption of methylene blue dye using groundnut shell and sorghum husks and the isotherm model used are Langmuir's Freundlich and Temkin isotherm.

Justification

Massive amount of groundnut shell and sorghum husk are readily available to be used as potential material for adsorption instead of being disposed and causing environmental pollution.

MATERIALS AND METHODS

Adsorption isotherms

Isotherms give an equilibrium relationship between the amounts of adsorbate adsorbed on the adsorbent surface and its concentration in the solution at a constant temperature. Numerous adsorption models are available in the literature to fit the experimental adsorption data. In this study the data were fitted using Langmuir, Freundlich and Temkin models. Each of these models makes use of a parameter q_e (i.e., adsorption capacity per unit mass of the adsorbent at equilibrium) in mg/g.

$$q_e = (C_0 - C_e) V / X \quad (1)$$

C_0 = Initial concentration of solution (mg/l)

C_e = Equilibrium concentration of solution in (mg/l)

V = Volume of the solution used

X = Mass of the adsorbent used

Langmuir isotherm model

Langmuir isotherm model assumed monolayer adsorption (the adsorbed layer is one molecule in thickness) with adsorption can only occur finite (fixed) number of definite localized sites that are identical and equivalent with no lateral interaction and steric hindrances between the adsorbed molecule even on adjacent sites, in other words, sorption occurs in a specific homogeneous site within the adsorbent site of the sorbents are identical and energetically equivalent. In its deviation, Langmuir isotherm refers to the homogeneous sorption which each molecule possesses a contact enthalpy and sorption activation energy (all sites possess the equal affinity for the adsorbate). With no transmission of adsorbed in place of surface. Graphically it is characterized by a plateau at equilibrium saturation point where one molecule occupies a site, no further adsorption can take place. The Langmuir isotherm is widely used and has found a successful application in many real sorption processes. Moreover, Langmuir theory has related rapid decrease of the intermolecular attractive forces to the rise of distance [3].

The linear form of Langmuir expression:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0}$$

Where

C_e is the equilibrium concentration of dye solution (mg/L),

q_e is the equilibrium capacity of dye on the adsorbent (mg/g),

q_0 is the monolayer adsorption capacity of the adsorbent (mg/g),

b is the Langmuir adsorption constant (L/mg) and is related to the free energy of adsorption.

The essential characteristic of Langmuir isotherm is expressed in terms of dimensionless constant separation factor or equilibrium parameter R_L , is defined as:

$$R_L = 1 / (1 + bC_0)$$

Where, C_0 is the initial adsorbate concentration (mg/g) and b is the Langmuir constant (L/mg). In the context, lower R_L values reflect the adsorption is more favorable. In deeper explanation, R_L value indicates the adsorption nature is either unfavorable ($R_L > 1$), Linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Freundlich isotherms

A Freundlich isotherm is a mathematical equilibrium between a fluid and a solid material. The Freundlich expression is a mathematical equation between an empirical expression representing the isotherm variation of liquid or gas on a solid material. The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below unity implies chemisorption process where $1/n$ above one is an indicative of cooperative adsorption. Its linearized and non-linear.

The linear form can be written as:

$$\ln q_e = \ln k_f + \left(\frac{1}{n} \right) \ln C_e$$

Where, k_f and n (dimensionless constants) are the Freundlich adsorption isotherm constants, which indicate the capacity and intensity of the adsorption, respectively.

Temkin isotherm model

Temkin isotherm assumes that the adsorption heat of all molecules decreases linearly with the increase in the coverage on the surface of the adsorbent.

The general form of Temkin equation is given below.

$$q_e = \frac{RT}{b_T} \ln A_T C_e$$

The linear form equation is written as:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$$

The curve is obtain by plotting q_e against $\ln C_e$, with A_T as Temkin isotherm equilibrium binding constant (L/g), b_T Temkin isotherm constant R, is universal gas constant (8.314 J/mol K) and T, is temperature [4].

Groundnut shell

Groundnut botanically known as *Arachis hypogea* belongs to Leguminosae family. A complete seed of groundnut is called the pod and the outer layer is called the shell. Brian George et al. investigate the groundnut shell fibers was found to be 38 mm and 0.2 mm diameter. Average tenacity of groundnut shell fiber is of 1.06 g/den. Also, average strain of the fibers was found to be 7.45 percent and average modulus 25.3 g/den (Figure 1) [5].



Figure 1: Groundnut shell.

Sorghum husk

Sorghum husk is an agricultural waste from milling of guinea corn (*Sorghum vulgare*), guinea corn is an important food crop grown abundantly in northern part of Niger and Benue Rivers in Nigeria [6] (Figure 2).

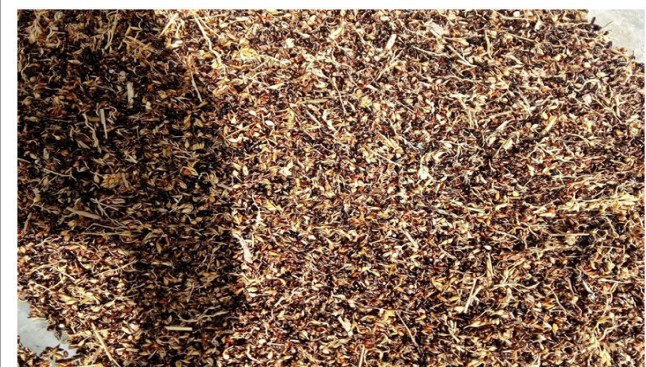


Figure 2: Sorghum husk.

Chemical

Methylene blue dye chemical was used for the initial adsorption experiments. Other chemicals such as NaOH and HCl were used to keep the pH constant. The adsorbents used were groundnut shell and sorghum husk [7].

Apparatus:

- Graduated cylinder
- UV spectrophotometer
- Beaker
- Orbital shaker
- Separating funnel
- Sieve
- Distilled water
- PH meter
- balance

Preparation of the adsorbent: Adsorbents (groundnut shell and sorghum husk) were collected from Sabon kauras Bauchi local government areas Bauchi state. The agricultural by product were washed and dried at low temperature (<105°C) for 48 hours to remove moisture content. After the drying process material were ground to fine powder and sieved through 600 µm size. The adsorbents is then used for the research work [8].

Procedure for adsorption isotherm studies: 50 ml of methylene blue solution of concentrations 10 mg/Ls 20 mg/Ls 30 mg/Ls 40 mg/L and 50 mg/L were prepared. 4.0 g of groundnut shell of the prepared sample was taken in to conical flasks containing the solutions with a known initial concentration and the solution was maintained at a constant pH and stirred until equilibrium concentration is reached. The equilibrium concentration is recorded and used for the Isotherm study. The same procedure was used to carry out the same experiment using 3.6 g of sorghum husk and methylene blue dye solution [9-11].

RESULTS AND DISCUSSION

This section presents the results and discussions of the research (Table 1). The following data were used:

Volume of the solution used=50 ml

Mass of sorghum husk used=3.6 g

Mass of groundnut shell used=4.0 g

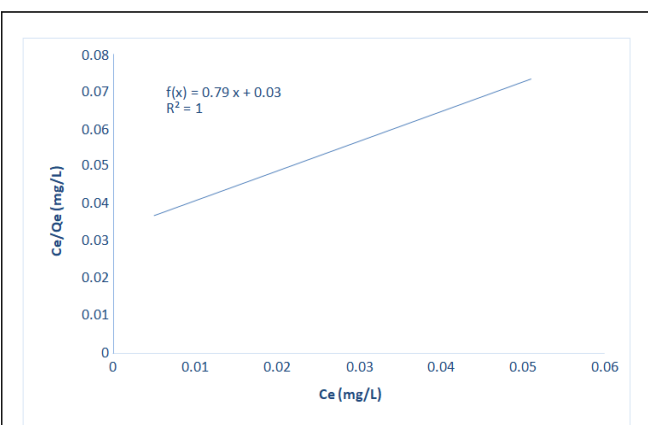
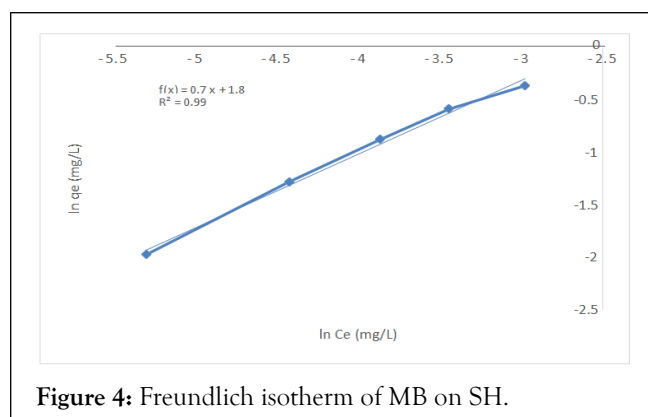
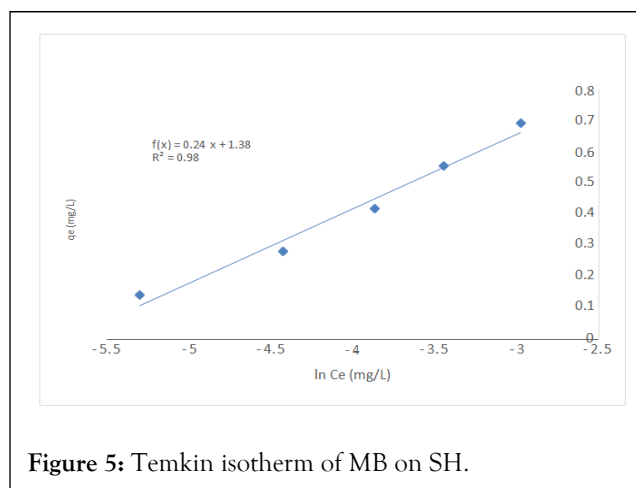
Table 1: Data obtained from adsorption of methylene blue on Sorghum husk.

C_0 (mg/L)	C_e (mg/L)	q_e (mg/g)	C_e/q_e (g/L)	$\ln q_e$ (mg/L)	$\ln C_e$ (mg/L)
10	0.005	0.138889	0.036	-1.97408	-5.29832
20	0.012	0.277778	0.0432	-1.28093	-4.42285
30	0.021	0.416667	0.0504	-0.87547	-3.86323
40	0.032	0.555556	0.0576	-0.58779	-3.44202
50	0.051	0.694444	0.07344	-0.36464	-2.97593

Methylene blue adsorption on Sorghum husk

The Langmuirs Freundlich and Temkin isotherm study for methylene adsorption on Sorghum husk was carried out. The Langmuirs Freundlich and Temkin plot were given in Figures 3-5 respectively.

The value of q_e is calculated using equation (1) and the values needed for the calculation of isotherms were recorded in table above.

**Figure 3:** Langmuir isotherm plot of MB on SH.**Figure 4:** Freundlich isotherm of MB on SH.**Figure 5:** Temkin isotherm of MB on SH.

From the Langmuirs Freundlich and Temkin isotherm plot of methylene blue removal on sorghum husks R^2 values of Langmuir constant was 0.99700 which is higher than R^2 value of Freundlich and Temkins this means that Langmuir data fitted well than Freundlich (0.983) and Temkin (0.9758) data in the adsorption process and that shows that the process is a monolayer adsorption process.

Methylene blue adsorption on groundnut shell

The Langmuirs Freundlich and Temkin isotherm for methylene blue adsorption on groundnuts shell was carried out. The Langmuirs Freundlich and Temkin plots are given in Figures 6-8 respectively.

The value of q_e is calculated using equation (1) and the values needed for the calculation of isotherms were recorded in Table 2.

Table 2: Data obtained from adsorption of methylene blue on groundnut shell.

C_e (mg/L)	Q_e (mg/L)	C_e/Q_e (g/L)	$\ln C_e$ (mg/L)	$\ln Q_e$ (mg/L)
0.011	0.138736	0.079287	-4.50986	-1.97518
0.032	0.277333	0.115385	-3.44202	-1.28254
0.055	0.415903	0.132242	-2.90042	-0.8773

0.076	0.5545	0.13706	-2.57702	-0.58969
0.121	0.692764	0.174663	-2.11196	-0.36707

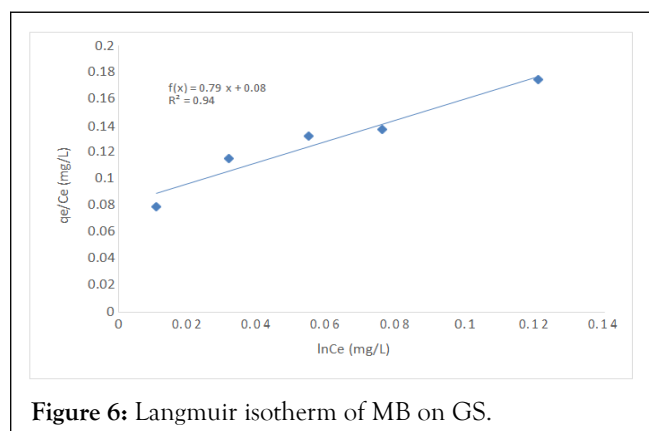


Figure 6: Langmuir isotherm of MB on GS.

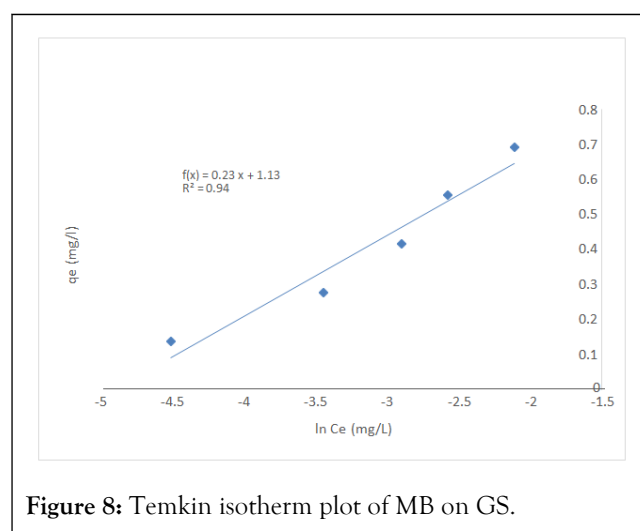


Figure 8: Temkin isotherm plot of MB on GS.

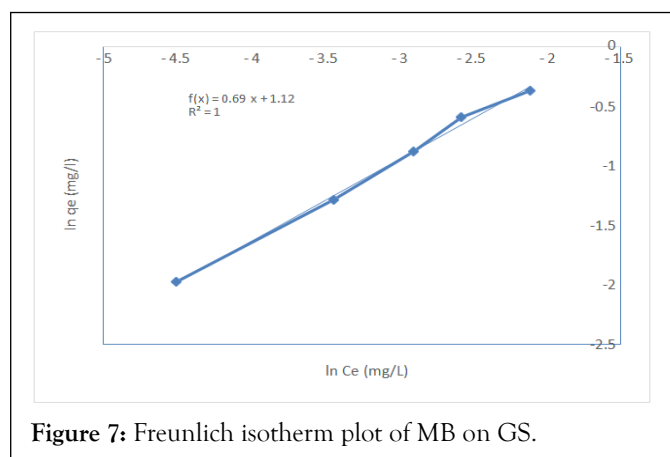


Figure 7: Freundlich isotherm plot of MB on GS.

From the above Langmuirs Freunlich and Temkin isotherm plot of methylene blue removal on groundnut shells R^2 value of Freundlich constant is 0.960 which is higher than R^2 value of Freundlich and Tebkins this means that Langmuir data fitted well than Langmuir (0.9436) and Temkin (0.944) data in the adsorption process. That shows that the adsorption process is multilayer adsorption process (Table 3).

Table 3: Langmuir isotherm constant.

	MB+GS	MB+SH
Qo (mg/g)	1.2583	1.259
b (L/mg)	9.9135	22.14
R^2	0.5436	0.97

For Langmuir isotherm; a plot of C_e/q_e was plot against C_e which indicate a homogeneous adsorption distribution of Langmuir isotherm. The values of b and Qo were obtained from the intercept and the slope of the graph (Table 4).

Table 4: Freundlich isotherm constant.

	MB+GS	MB+SH
K_f (mg/g)	3.066	2.931
$1/n$	0.6881	0.1734
n	1.4533	1.3624

R^2	0.9601	0.9758
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From the Freundlich constants (Table 5) the values of n are found to be greater than one ($n > 1$) indicating that the adsorption is a physical process. The values of n ranges from 1-10 represent good adsorption process.

Table 5: Temkin isotherm constant.

	MB+SH	MB+GS
A_T	1	1
b_T	10353.7	10793
R^2	0.976	0.944

The Temkin binding energy (b_T) is positive for all the experiments indicating that the process is endothermic.

CONCLUSION

For the adsorption of methylene blue on sorghum husks Langmuir isotherm is more suitable to fit the experiment data because it has R^2 value of 0.9710 value than the other models while for the adsorption of methylene blue on groundnut shells Congo red on sorghum husk and Congo red on groundnut shells Freundlich isotherm fitted well the experimental data due to high R^2 values of 0.960s 0.983 and 0.9720 respectively. The Temkin binding energy (b_T) are positive for all the experiments indicating that the process is endothermic.

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