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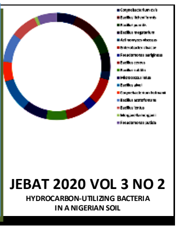

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HYDROCARBON-UTILIZING BACTERIA IN A NIGERIAN SOIL

Adsorption Equilibrium and Kinetic Studies of Methylene Blue Dye Using Groundnut Shell and Sorghum Husk Biosorbent

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ABSTRACT

The Groundnut Shell (GS) and Sorghum Husk (SH) was used as an adsorbent for adsorption of Methylene Blue (MB) dye. The adsorbent was characterized using FTIR and Proximate analysis, Fourier transforms infrared spectroscopy (FTIR) spectrum showed the presence of absorption bands typical of a plant-based biomaterial. The effects of various experimental parameters, such as initial dye concentration, and contact time on the adsorption extent were investigated. The results showed that the percentage removal of MB dye was increased by increasing the concentrations of dye. The dye concentration was determined by spectrophotometry. Langmuir, Freundlich, Temkin and Harkins and Jura models were used to representing the equilibrium data. The Langmuir model was more adequate to represent the equilibrium data for MB with GS, whereas the Temkin model fitted well to both GS and SH for MB. The maximum adsorption capacity was found to be 7.052 mg/g and 15.3846 mg/g for GS and SH, respectively with MB dye. Adsorption data were modelled using the pseudo-first and pseudo-second-order kinetic equations, power function and Elovich models. It was seen that the pseudo-second-order kinetic equation could best describe the sorption kinetics for all the adsorption processes. It was concluded that GS and SH adsorbent can be utilized as an efficient low-cost adsorbent for removal of Methylene Blue dye.

INTRODUCTION

Dyes are synthetic aromatic compounds, which have various functional groups. Some dyes and their degradation products may be carcinogens and toxic, and consequently, their treatment cannot depend on biodegradation alone [1]. Therefore, extensive research has been conducted to find an effective and efficient alternative for the removal of dyes [2]. Methylene Blue (MB) is a basic dye that is the most common among all other types of dyes category and it is extensively used in the textile operation. It is also used in some medical treatments [3]. Therefore, the removal of Methylene Blue from effluents is essential to protect human, animals and water resources. Various technologies together with the advantages and disadvantages applied for the treatment of dye effluents were extensively reviewed [4]. Adsorption is a physical-chemical treatment of wastewater in which the dissolved molecule is attached to an adsorbent surface using physical and chemical properties. Depending on the nature of the adsorbent and the origin of the dyes, different interactions may be performed, such as electrostatic interaction and Vander Waals forces [5]. The use of agricultural solid waste (due to its widespread availability and low cost) for the treatment of dye effluents is not only essential to the environment in clearing the solid waste disposal problems to farmers and agro-industries but also the economy. Disposal of these agricultural residues is secondary environmental pollution. This increases the researchers' interest to produce porous adsorbent that can be derived from an agricultural origin for removing different types of dyes from industrial effluents. Agricultural biomass is not only abundantly, but also cheap and renewable natural material [6]

MATERIALS AND METHODS

Reagents

All reagents are of analytical grade unless stated otherwise.

Equipment/Instruments

FT-IR Spectrophotometer (Perkin Elmer, version 10.03.06) Microwave Oven (Gen Lab., OV/100), Electronic Weighing Balance (ADAM Equip., PW184), Orbital Shaker (Stuart SSL1), U.V Visible spectrophotometer (CECIL CE7400), Digital pH Meter (HANNA INST. PH209), Muffle Furnaces (Vecstar Ltd, EC F2)

Adsorbent Collection and Preparation

The raw groundnut shell and sorghum husk were collected in Gombe town, Gombe State, Nigeria. This agricultural waste was washed thoroughly with water to remove sand, dirt and other impurities present in it and then dried in an oven at 55 0C for 24 h, until all moisture contents were removed. It was then gronded in a mill and sieved in a sieve shaker of particle size 80 µm. The raw groundnut shell and sorghum husk powder that passed through the sieve were stored in an airtight container and used as adsorbent without any further pretreatment.

Preparation of Adsorbent Solutions

Analytical grade Methyl blue (MB) dyes were obtained from a Biochemistry laboratory, Gombe State University. A stock solution of dye of concentration 1000mg/l was prepared by dissolving 1 g of powdered dye in 1 L of distilled water. An experimental dye solution of desired concentration was obtained by appropriate dilution of the stock solution [7].

Adsorbent Characterization

Fourier transform infra-red (FTIR) spectrophotometer was used to identify the different functional groups available on the adsorbent sites. The FTIR of the adsorbent will be taken before adsorption using FTIR spectrophotometer. 0.1 g of each adsorbent will be encapsulated with 1 g of KBr spectroscopy grade and by introducing the mix in a piston's cell of a hydraulic pump with compression pressure 15 KPa/cm2; the solid translucent disk will be obtained which will introduce in an oven for 4hrs at 1050C to ensure the non-interference of any existing water vapors or CO2 molecules. The FTIR spectrum will then be record within the wave number range 4000 – 450 cm-1 [7].

Proximate Analysis

The proximate analysis determines the moisture content, volatile matter content, ash content, and fixed carbon. The first three were determined in laboratory and the fixed carbon was calculated by difference.

Determination of Moisture

Moisture can be removed by air-drying but the inherent moisture can only be removed completely by drying in an oven at 1050C for about an hour. The added amount of free and inherent moisture is called total moisture. 250 mL beakers are cleaned and dried. The weight of the beaker is taken, and one gram of each sample is weighed in the beaker (W1). Then it is heated in an electric oven out of contact with air (to avoid oxidation) at 1050C temperature for an hour. After heating, the beaker was transferred to a desiccator and rapidly reweighed (W2). The difference in weight (i.e., W1 - W2) gave the amount of moisture. Moisture content is expressed in percentage [8].

Determination of ash content

The residue left after burning is known as ash. It is generally composed of inorganic substances.1 gm of powdered GS and SH is weighed in a crucible (W1). Then the crucible is kept inside a muffle furnace and the temperature is gradually raised up to 800 0C. At 800 0C the temperature is kept constant and the incineration of the sample is completed by heating for an hour at that temperature. After incineration, the crucible is allowed to cool and transferred to desiccators. Then the basin (crucible) is re-weighed (W2). Deduction of W1 (weight of the basin) from W2 (weight of the basin + ash) gives the amount of ash in the sample. Ash content is expressed in percentage [8].

Determination of volatile matter

The volatile matter, sometimes called volatiles consists mainly of the gases and water and tarry vapours evolved from the sample when it is heated at high temperature. To determine it, 1 gm of sample is taken in a crucible. The weight of the silica crucible and a sample is W1. The sample is then heated for 7 minutes at a constant temperature of 925 0C inside a furnace. After heating, the crucible is cooled and transferred to desiccators. After few minutes the silica crucible is re-weighed (W2). The difference between W1 and W2 gives the amount of apparent volatile matter in the sample. The actual volatile matter is obtained after deducting the moisture content of the sample. Volatile matter content is expressed in percentage [8].

Calculation of fixed carbon (F.C.)

The fixed carbon represents the carbon content in a sample that has not combined with any other element (in a free state). The amount of fixed carbon is computed by subtracting the sum of the percentage of moisture, volatile matter and ash from hundred.

Fixed carbon = 100 - (moisture % + ash % + volatile matter %) [8].

Phytochemical Analysis

Test for Flavonoids

2ml of the filtered sample was dissolved in 10 % NaOH of solution to give a yellow colour. A change in colour from yellow to colourless on addition of dilute hydrochloric acid indicates the presence of flavonoids [9].

Test for Steroid

To small amount of the extract, 2 mL of chloroform was added then a volume of conc. H2SO4 was added by sides. The turning of red in the upper layer and yellow with green fluoresence in the sulphuric acid layer indicates the presence of steroid [9].

Test for Glycoside

To 5 mL boiling distilled water 1 g of the bark was added, stirred and then filtered through filter paper. Few drops of conc. HCl were added to 2 mL portion of the filtrate. It was boiled for few minutes to hydrolyse any glycosides present, few drops of aqueous ammonia solution were added to make the mixture alkaline. Then three drops of the mixture were added to 2 mL of Benedict's reagent and boiled. A reddish brown indicates the presence of glycosides [9].

Test for Saponin

1 mL of the extract was shaken with distilled water in a test tube, frothing which persists on warming indicates the presence of saponin [9].

Test for Tannins

Small quantity of the extract was mixed with distilled water and heated on a water bath. The mixture was filtered while Conc. H2SO4 and 5 % ferric chloride were added to the filtrate. A blue-black, green or blue-green precipitate indicates the presence of [9].

Test for Alkaloids

2 mL of the extracts was stirred with 5 mL of 1 % aqueous hydrochloric acid on water bath and filtered. Few drops of Dragendorff's solution was added to the filtrate, the presence of orange red precipitate indicates the presence of alkaloids [9].

Batch Adsorption Experiment

Batch adsorption of MB dyes onto the adsorbent groundnut shell and Sorghum husk was conducted in a 250 mL airtight Erlenmeyer flask containing 200 mL of known concentration of the dyes solution and an accurately weighed amount of the optimum adsorbent dosage of 4 g and 3.6 g for GS and SH respectively [10]. The mixtures in the flasks were agitated on a mechanical shaker operating at a constant speed of 200 rpm. The effect of contact time (30, 60, 90, 120 &150 min), and initial dye concentration (10, 20, 30, 40 & 50 mg/l), at constant temperature of 37 °C was evaluated. The flask containing the samples was withdrawn from the shaker at a predetermined time interval, filtered and the final concentration of the dyes in the supernatant solutions was analyzed using the UV-visible spectrophotometer. The pH of the solution was adjusted using 1M HCl or NaOH to the optimum pH of 3.0 [10]. The amount of equilibrium uptake of the dyes was determined using (equations **1** and **2**):

$$q_e = \frac{(C_o - C_e)V}{M} \qquad \ldots \quad (1)$$

$$\%Dye\ Removal = \frac{(C_o - C_e)V}{M}\ X\ 100 \qquad \ldots \quad (2)$$

Where q_e is the amount of dye taken up by the adsorbent at equilibrium (mg/g), C_o is the initial dye concentration (mg/l), C_e is the dye concentration at equilibrium (mg/l), M is the mass of the adsorbent (g), and V is the volume of the solution, (L).

Equilibrium adsorption Experiment

Equilibrium adsorption experiments were conducted at average room temperature. Predetermined volume of dye solution will be added to 250 mL stoppered Erlenmeyer flasks containing appropriate mass of Groundnut shell and Sorghum husk powder and agitated on mechanical shaker at 200 rpm. Portions of residual dye samples were removed from the flasks periodically and filter. The absorbance of the residual dye was read at the maximum wavelength of 665 nm and scanned using UV/visible spectrophotometer. The residual dye, q_e (mg/g), was calculated from the equation 2 above.

The kinetics experiments were conducted by similar to those for batch adsorption.

The adsorption kinetic data was assessed using four models: Pseudo First Order, Pseudo Second Order, Elovich and Power Function Kinetics Equations as stated in equations **3, 4, 5, 6** and **7**, respectively.

kinetics equation based on concentration of solution and adsorption capacity of solid, Lagergren's first order rate equation has been called pseudo-first order. The linear form of the pseudo-first-order kinetic mode is represented by: [7]

$$\ln(q_e - q_t) = lnq_e - k_1 t \qquad \ldots \quad (3)$$

Where qe and qt are the values of amount of the dye adsorbed per unit mass on the adsorbent at equilibrium and at various time t, respectively, k1 is the Pseudo-first-order adsorption rate constant (min-1). The values of k1 and calculated qe can be determined from the slope and intercept respectively, of the linear plot of ln (qe – qt) versus t.

The pseudo-second-order kinetic model is expressed by: [7].

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} \qquad \ldots \quad (4)$$

Where k_2 is the pseudo-second-order adsorption rate constant (g/mg.min) and q_e is the amount of dye adsorbed (mg/g) on the adsorbent at equilibrium. The initial adsorption rate, h (mg/g.min) is expressed as: [11].

$$h = k^2 q_e \qquad \ldots \quad (5)$$

The plot of t/qt versus t gives a linear relationship which allows computation of k_2, h and calculated q_e. Among these models, the criterion for their applicability is based on judgment on the respective correlation coefficient (R^2) and agreement between experimental and calculated value of q_e, [12].

Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate-adsorbent [12]. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation. The linearized form of Elovich kinetic equation (model) is expressed by [12];

$$q_t = \frac{ln(\beta\alpha)}{\beta} - \frac{lnt}{\beta} \qquad \ldots \quad (6)$$

Where: α is the initial adsorption rate (mg.g-1.min-1) and β is the desorption constant (mg.g^{-1}min) if the adsorption fits the Elovich model, a plot of qt versus ln (t) should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)$ ln $(\beta\alpha)$.

The power function kinetic equation (model) is represented by:

$$logq_t = \log a + b \log t \qquad \ldots \quad (7)$$

Where: the constant, a, represents the initial rate (mg.g^{-1}.min^{-1}) and the constant b represents the rate constant of the reaction (g/mg/min). If the adsorption fits the power function model, a plot of log q_t versus log t should yield a linear relationship with a slope of b and intercept log a [13].

RESULTS AND DISCUSSION

The Brunauer Emmet Teller (BET) surface area measurement technique was used to find the characteristics of the sample. Pore volume and pore volume distribution of adsorbents play an important role in adsorption [14]. The BET surface analysis for the unmodified sorghum husk has a surface area of 139.539 m^2/g, the pore volume of 0.053 cc/g, pore width of 2.647 nm, micropore surface area of 180.937 m^2/g whereas the unmodified groundnut shell has a surface area of 302.522 m2/g, the pore volume of 0.091 cc/g, pore width of 2.647 nm, micropore surface area of 326.976 m^2/g [10].

Fourier Transform Infra-Red (FTIR) Spectroscopy

The FTIR spectral of SH and GS powder obtained within the spectral range of 4000-450 cm^{-1} as shown in **Figs. 1** and **2** respectively, displayed the characteristics peaks of the correspondent adsorbent such as prominent peak at 3477.79 cm^{-1} and 3450.68 cm^{-1} for SH and GS respectively due to hydroxyl group, O-H bond, probably attributed to adsorbed water. The peaks at the region of 2925.84 cm^{-1} SH and 2925.44 cm^{-1} GS were attributed to C-H interaction with the surface of the adsorbent indicating the carbon dioxide of normal air. The peak at 1642.67 cm^{-1}and 1633.29 cm^{-1} for SH and GS respectively shows the presence of C=C bond from alkenes. The characteristics band at 1033.57 cm^{-1} SH and 1032.71cm^{-1} GS corresponds to C–O bond, confirming the presence of carboxylic acid [15,10].

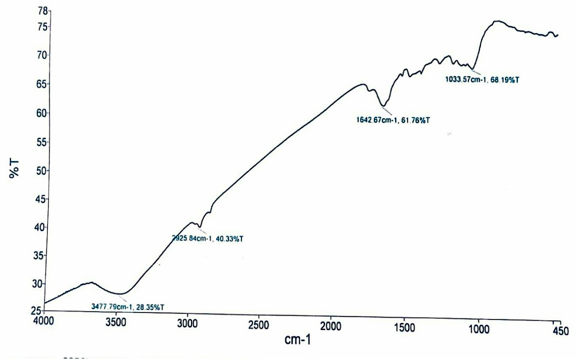

Fig. 1. FTIR spectrum of sorghum husk.

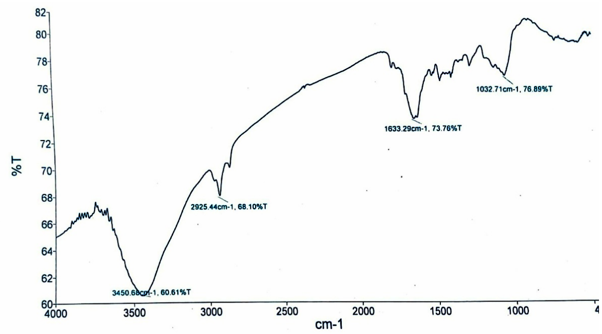

Fig. 2 FTIR spectra of groundnut shell.

Proximate Analysis

The result of the proximate compositions of the adsorbent samples is presented in **Table 1**. The moisture, volatile matter, ash and fixed carbon content of the adsorbent were: 7.63, 3.124, 11.97 and 77.276%, respectively for GS and the moisture, volatile matter, ash and fixed carbon content of the adsorbent were: 7.07, 13.824, 15.85 and 63.256%, respectively for SH.

Table 1. Proximate analysis of groundnut shell and sorghum husk.

	moisture %	ash %	volatile matter %	fixed carbon %
groundnut shell	7.63	11.97	53.124	27.276
sorghum husk	7.07	15.85	45.824	31.256

Phytochemical Screening

The result of the phytochemical screening of the adsorbent samples is presented in Table 3. The Phytochemical analysis was done qualitatively, the plus (+) sign indicating the present of the respective phytochemical parameter in very small amount and (+++) in large amount whereas the negative (-) sign indicating the absent of the respective phytochemical parameter.

Table 2. Phytochemical analysis of groundnut shell and sorghum husk.

phytochemicals	groundnut shells	sorghum husk
alkaloids	+	+++
saponins	-	-
tannins	-	-
steroids	+	-
glycosides	-	-
flavonoids	-	-

Effect of initial dye concentration

The percentage removal of dye is widely dependent on the initial dye concentration. The impact of the initial dye concentration factor depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface. **Fig.** 3 illustrates the percentage removal for MB dye, versus the initial dye concentrations (10–50 mg/L) onto GS and SH at room temperature. It is clear that the percentage removal for MB increased from 89.86% to 97.55% for GS and SH, respectively.

The increase in initial dye concentration enhances the interaction between dye and adsorbent. In another word, increase in the initial dye concentrations increase the driving force to overcome the resistance of the mass transfer of dye between the solution and the adsorbent [7]. Furthermore, it can be seen that with an increase of dye concentration from 10 to 50 mg/L, the adsorption capacity (q_e) increases from 0.063 to 2.137 mg/g. This is due to the higher adsorption rate and utilization of all active sites available for the adsorption at higher concentration.

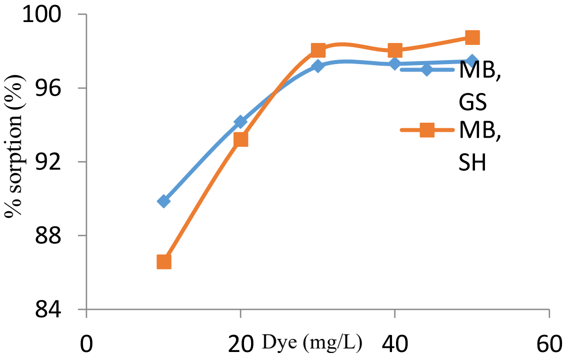

Fig. 3. Effect of initial dye concentration for methylene blue onto groundnut shell and sorghum husk.

Effect of contact time for Methyl Blue Dye

Contact time is an important parameter in the adsorption process. The effect of contact time on the removal of MB dye on to GS and SH is depicted in **Fig.** 4. It can be observed that there was a rapid removal in the first minutes and it proceeds slowly until optimum adsorption (equilibrium time) at 90 minutes for GS and 120 minutes for SH. Similar result has been reported for the adsorption of MB onto Neem leaves powder [7]. It can be inferred from the rapid sorption rate at the initial stages that there was abundance of active sites on the external surface of the biosorbent which resulted in the rapid MB dye removal.

The slower rate of removal at the later stages can be attributed to the diffusion of the dyes into the interior part of the adsorbent since the external surface has been occupied by the molecules of the dye. Once equilibrium is attained, there was no further increase due to the fact that the remaining vacant sites are difficult to occupy probably caused by repulsive forces between the molecules on the adsorbents and the bulk phase [16].

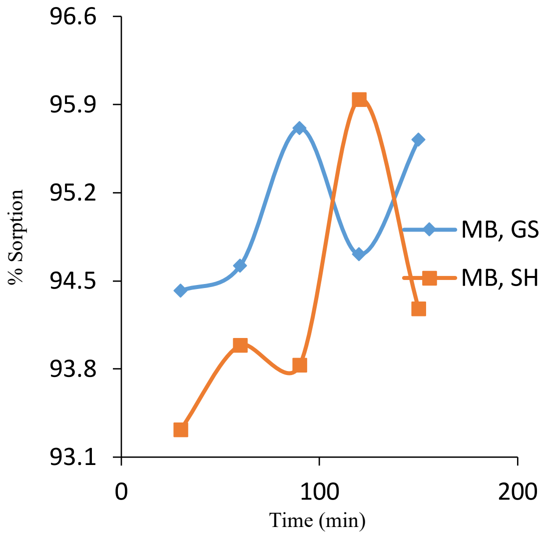

Fig. 4. Effect of contact time for methylene blue onto groundnut shell and sorghum husk.

Calibration Curves

The UV/VIS spectrophotometer was used to determine the concentration of MB in solution at a maximum absorption wavelength, λmax. This was determined by varying the wavelength of the spectrophotometer from 400nm to 1100nm.The maximum wavelength of the Spectrophotometer for the determination of the absorbance of MB was found to be 665nm. All the absorbance measurement for MB were carried out using a UV/VIS Spectrophotometer set at the maximum wavelength, λmax of 665nm.

A calibration curve was plotted between absorbance and certain concentrations of dye solution. Unknown MB concentrations were measured using calibration curve. In order to obtain the standard calibration curve 5 samples of different concentrations 10, 8, 6, 4 and 2 mg/l were prepared for MB. The absorbance of each sample was then measured at their respective maximum wavelength. The absorbance was plotted against the concentrations to obtain a standard calibration curve for each dye as in **Fig. 5**.

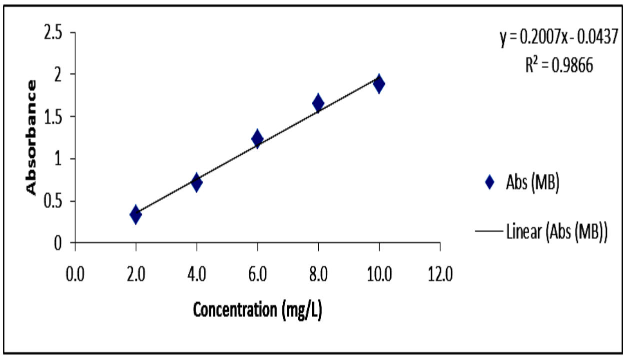

Fig. 5. Standard calibration curve for MB.

Equilibrium isotherm models

Adsorption isotherms are important in describing the mechanism of adsorption for analyzing the interaction of dyes on the surface of adsorbent. **Figs. 7** to **10** described the Langmuir, Freundlich, Temkin and Harkins & Jura adsorption isotherms respectively for MB removal using GS and SH. The values of distinctive parameters for the Langmuir, Freundlich, Temkin and Harkins & Jura models for MB removal using GS, and SH were given in **Table 3**. The best fitting order of these models is conformed to be Langmuir >Freundlich>Temkin: for GS and Temkin>Freundlich> Langmuir: for SH. Langmuir isotherm model fitted the results quite well for removal of MB dye by GS (**Table 3**) suggesting that:

1. the surface of the sorbent is homogenous,
2. all sites are energetically equivalent, and each binding site accepts only one MB dye molecule,
3. the adsorbed molecules are organized as a monolayer and
4. no interaction between adsorbed molecules.

Similar observations were reported in the MB dye removal by Raw Corn Corbs (RCC) Powder [7]. **Table 3** also showed that the correlation of the experimental results was obtained fitted with the Freundlich isotherm model with GS and SH with 0.97 and 0.82 respectively, and it also confirmed favorable from n values <1 which indicates a chemical process.

Table 4 and **Fig. 6** showed that the best correlation of the experimental results was obtained with the Temkin isotherm model with SH; the Temkin isotherm equation explicitly takes into the account of adsorbent-adsorbate interactions by ignoring the extremely low and large value of concentrations. It assumes that the heat of adsorption of all the molecules in layer decreases linearly rather than logarithmic with coverage due to adsorbent-adsorbate interactions [17].

The constant B is less than 8 kJ/mol, it indicates a weak interaction between the adsorbate and adsorbent hence such adsorption can be expressed as physical adsorption, [18]. The Harkin and Jura Isotherm did not provide a good fit to the experimental data. The Harkin and Jura constants, A, B and the correlation coefficients R^2 for MB are given in Table 8. The plot of 1/qe2 against log Ce **Fig. 7** was also nonlinear with low R2 suggesting that it was not appropriate for describing the adsorption of MB onto GS & SH powder.

Table 4. Equilibrium isotherms parameters.

Model	Parameters	GS	SH
Langmuir	q_m (mg/g)	7.052	15.385
	K_L (l/mg)	0.032	0.2089
	R^2	0.997	0.8879
Freundlich	K_f	0.795	5.3700
	n	0.320	0.8634
	R^2	0.974	0.8920
	KT(mol/k)	1.300	3.9635
	B(kj/mol	4.0201	1.5536
	R^2	0.9688	0.9234
Harkin & Jura	A	0.2161	0.1134
	B	0.2932	-0.2226
	R^2	0.0581	0.4931

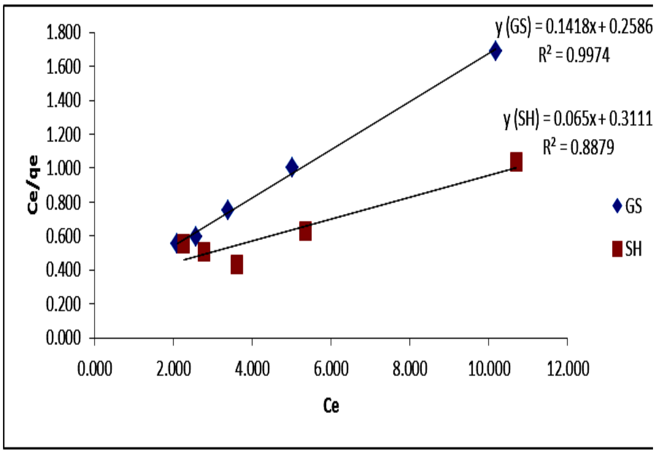

Fig. 6. Langmuir isotherm model.

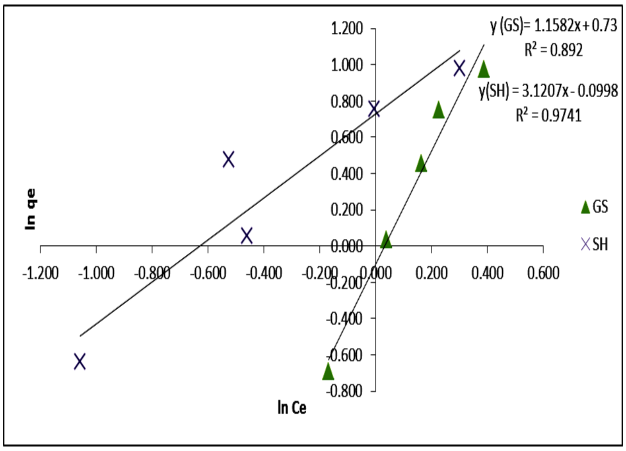

Fig. 7. Freundlich isotherm model.

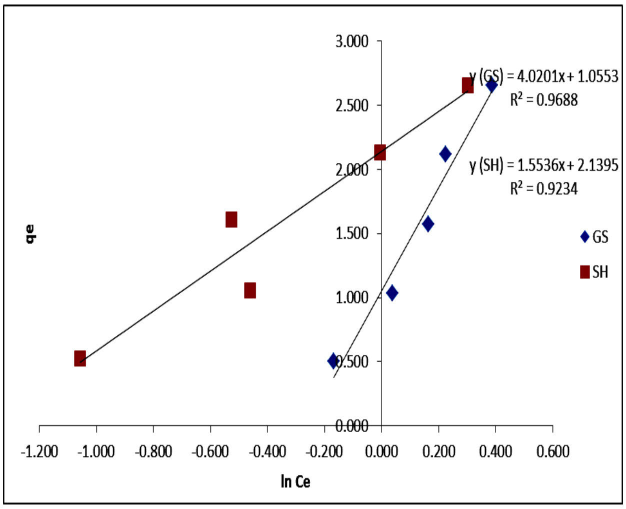

Fig. 8. Temkin isotherm model.

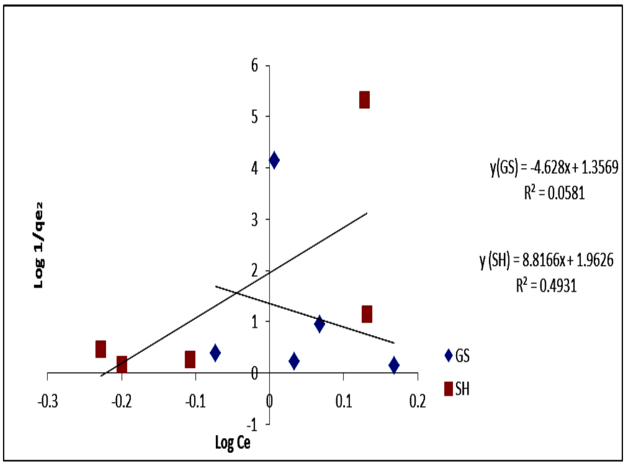

Fig. 9. Harkin & Jura isotherm model.

Kinetics model

Four kinetic models i.e., pseudo-first-order, pseudo-second-order, power function, and Elovich model as mentioned earlier were applied to study the reaction pathways and potential rate determining steps of the adsorption of MB dye onto GS &SH powder. The pseudo-first-order model did not provide a good fit to the experimental data. The first-order rate constant, K_1, the correlation coefficients, R^2 and the theoretical and experimental equilibrium adsorption capacity qe are given in **Table 4**. The plot of log (q_e- q_t) versus *t* **Fig. 10** was nonlinear with low R^2 0.389 and 0.286 for GS & SH respectively. Moreover, the theoretical and experimental equilibrium adsorption capacity q_e obtained from the plot did not agree (i.e., varied widely), suggesting the inadequacy of the pseudo-first-order model for describing the adsorption kinetics of MB dye onto GS & SH powder. However, the kinetic data was fitted well to the pseudo-second-order model.

The pseudo-second order rate constant K_2, the initial adsorption rate, H and the theoretical and experimental equilibrium adsorption capacity are given in **Table 4**. The plot of t/qt against t is depicted in **Fig. 11**. Contrary to the pseudo-first-order model, the fitting of the kinetic data in the pseudo-second-order model showed excellent linearity with high correlation coefficients, R^2 for both the adsorbent. In addition, there was a good agreement between the calculated q_e and the experimental q_e values (i.e., the q_e values were exactly the same for GS 2.165 mg/g and very close value for SH, 2.38 and 2.39 mg/g) indicating that the adsorption of MB by GS & SH powder followed the pseudo-second-order kinetics. Hence the adsorption process is controlled by chemisorption [17]. This suggests that the forming of interaction between the adsorbate and the adsorbent on the external surface of the adsorbent (film diffusion) is the rate determining step [19].

The power function model did not provide a good fit to the experimental data. The power function constants, a, b and the correlation coefficients, R_2 are given in **Table 5**. The plot of log q_t versus log *t* **Fig. 12** was nonlinear with low R^2 suggesting that the power function model was not appropriate for describing the adsorption of MB onto GS & SH powder. The Elovich model did not provide a good fit to the experimental data. The Elovich constants, α, β and the correlation coefficient R^2 are given in **Table 5**. The plot of q_t against ln *t* **Fig. 12** was also nonlinear with low R^2 suggesting that the Elovich model was not appropriate for describing the adsorption of MB onto GS & SH powder**.**

Table 4. Kinetic models parameters for MB.

Kinetic Model	Parameters	GS	SH
Psdeudo First Order	$q_{e,cal}$ (mg/g)	0.0783	0.1093
	$q_{e,\,exp}$ (mg/g)	2.6150	2.3980
	K_1 (min^{-1})	0.0042	0.0048
	R^2	0.3897	0.2858
Psdeudo Second Order	h(mg/gmin)	4.1490	2.4543
	$q_{e,\,cal}$ (mg/g)	2.6150	2.3980
	$q_{e,\,exp}$ (mg/g)	2.6150	2.3980
	K_2(g/mg min)	0.7790	0.6583
	R^2	0.9999	0.9996
Elovich	β	-39.37	-56.81
	α	2.85E10	2.4E15
	R^2	0.4208	0.4621
Power Function	a	2.5206	2.2485
	b	0.0068	0.0108
	R^2	0.4631	0.4241

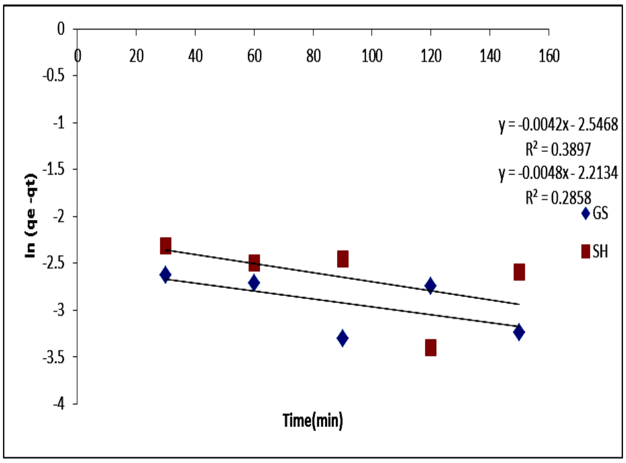

Fig. 10. Pseudo first order kinetic model.

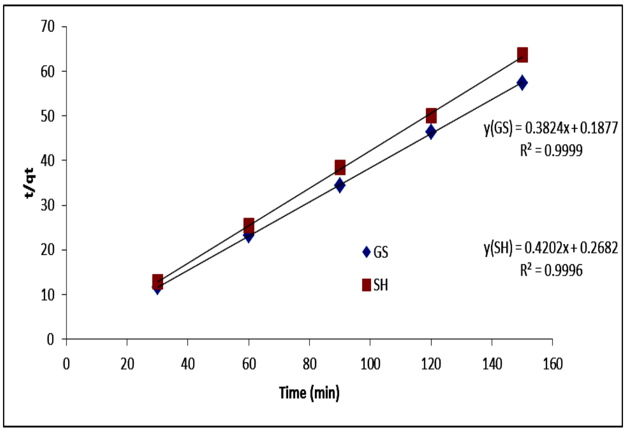

Fig. 11. Pseudo second order kinetic model.

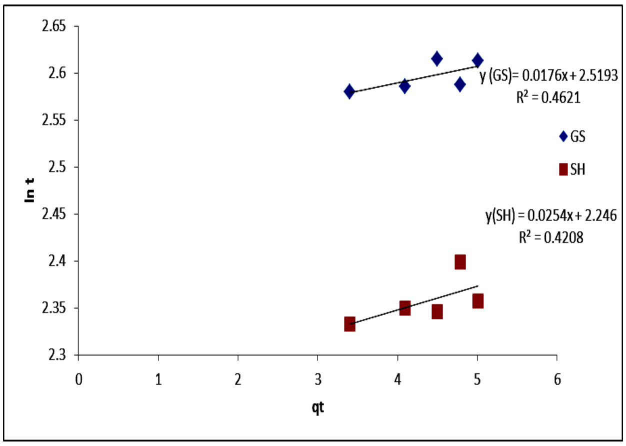

Fig. 12. Elovich kinetic model.

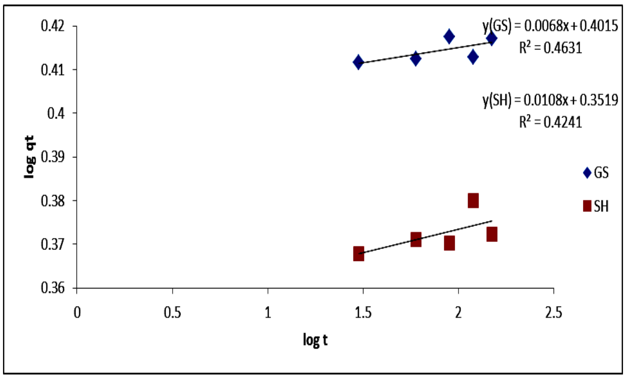

Fig. 13. Power function kinetic model.

CONCLUSION

In this research, the use of the agricultural waste to address the problem of dye loaded wastewater was addressed. For this purpose, two differently bio sorbent has been used successfully as an adsorbing agent for the removal of Methylene Blue MB from aqueous solutions. The adsorption was influenced by various parameters such as initial dye concentration, and time. The removal efficiency increased with increasing dye concentration of the process. The Langmuir, Freundlich, Temkin and Harkin & Jura adsorption isotherm models were used for the description of the adsorption equilibrium of MB dye onto GS and SH. The data were in good agreement with the Langmuir isotherm for MB onto GS and the Temkin Isotherm were in good agreement with all the adsorbent. It was shown that the adsorption of MB and CR onto two adsorbents was best fit the pseudo second order model for the evaluation of kinetic parameters of the adsorption process. However, since GS & SH, an agricultural solid waste was locally available, were used in this study, the adsorption process is expected to be economically viable for wastewater treatment

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