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REMOVAL OF METHYL ORANGE DYE FROM AQUEOUS SOLUTION USING GROUNDNUT (*Arachis hypogaea*) SHELL AS ADSORBENT

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Abstract

This work was conducted to determine the ability and effectiveness of groundnut shell to remove methyl orange dye from aqueous solution. The biomass (groundnut shell) was characterized for some physico-chemical properties, before it was used for adsorption studies. The results obtained indicated that the biomass has a positive surface charge with pH of 6.80 at point of zero charge. The results from fourier transform infra- red spectroscopy (FTIR) revealed that the biomass (GS) contain O-H, C-H, C-O, CH_2, C-O-C and C=O functional groups. The results from proximate analysis of the biomass showed that the groundnut shell has high content of fibre (cellulose, hemicellulose and lignin) as well as low moisture content. The GSA, was further used for the removal of methyl orange dye from aqueous under the influence of some adsorption variables. Data obtained revealed that increase in the Initial dye concentrations, increased the methyl orange removal efficiency. The optimum percentage color removal efficiency was obtained as 72% at 100gldm^3 of the initial dye concentration. However increase in pH increased color (methyl orange) removal efficiency. At pH 2-6, 3.653-6.738 mg/g of methyl orange was removed. The process was favoured by increase in adsorbent dosage evident to the (45.3 - 69.5%) of color removal efficiency when the adsorbent was varied (0.2g – 11.0g). Similarly, variations in temperature enhanced color removal. Optimum temperature for color removal was obtained at 50^{O}C with 69.6% color removal efficiency. Contact time (20 – 100) mins variations revealed 46.1 – 64.8% color removal efficiency. The experimental data were further subjected to some adsorption kinetics and isotherms to understand the mechanism of the process. The process was found to follow the Pseudo-second order kinetic model with a correlation coefficient of 0.9887 and K_2 of 0.0358 g/mg^{-1}. Also the Langmuir adsorption isotherm was better suited to describe the adsorption mechanism with a correlation coefficient of 0.9763, K_L of 0.051 and $q_m$of 2.96 mg/g. The free energy change ΔG from the thermodynamic studies revealed that the process is feasible and spontaneous, negative value of enthalpy change (ΔH) indicates an exothermic adsorption process and the positive and large value of entropy change (ΔS) reflects a high rate of disorderliness. The groundnut shell is a good adsorbent for the removal of methyl orange dye from aqueous solution.

Keywords: Thermodynamics, Methylorange dye, Groundnut shell

1.0 INTRODUCTION

Environmental problems are among daily life problems in Nigeria as in the world at large. Such problems are caused by the destruction of forests, erosion, rapid increase of population, distorting industrialization and decreasing green areas, distortion of shores, chemical used in industries, oil exploration and exploitation, industrial activities, technological development among others are ones that their solutions are searched not only in Nigeria but also in all over the world [1, 2, 3]. The discharge of waste materials into the environment is a global issue that has been emphasized by several environmentalist organizations. The usage of dyes in large quantities results in coloured effluent, which pollutes the

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environment. Coloured wastewater is discharged by the textile, paper, and food sectors, as well as tanneries and electroplating plants [4, 5]. Colour or dye, as one of the recalcitrant, persists in moving water for long distances, retards photosynthesis, and inhibits aquatic biota growth by blocking out sunlight and using dissolved oxygen [6]. In humans, several colours have been linked to allergic dermatitis, skin irritation, cancer, and mutation. Dye concentrations of less than 1 mg/L may cause noticeable coloration, resulting in public outcry [7, 8]. In order to eliminate colours from wastewater, several treatment methods such as biological, chemical, and physiochemical are utilized, however most of these processes have severe drawbacks such as the generation of harmful byproducts, a high energy need, or a high cost [9]. In this context, cost effective alternative technologies or sorbents for deletion of dyes are needed. Natural materials that are available in large quantities or certain waste products from industrial or agricultural operations may have potential as inexpensive sorbents [2]. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration [10]. The effectiveness of sorption for the removal of dyes has been shown in several studies [4, 11, 12, 9, 13, 5, and 14]. Thus, this work proposed to use a low-cost sorbent for dye removal.

2.0 MATERIALS AND METHODS

The chemical used were all analytical grades. The hydrochloric acid HCl (96-70.5 %, S.G 1.42 LOBA Chemie Lab Reagent and fine chemicals), and sodium hydroxide (99 % Fisher Scientific) used were of analytical grade. Hydrochloric acid (0.1 mol/L) and sodium hydroxide (0.1 mol/L) solutions were used for pH adjustment during the experiment. Laboratory test sieve (mesh no. 63µm Pascal Eng. Co. Ltd Sussex England, Serial No: 42729) was used to sieve the adsorbent. Fourier Transform Infra-Red Spectrophotometer (Bruker FTIR Laser class 1 Spectrophotometer absorption band range of 4000-400 cm) was used for functional group identification; the dye concentration was measured using UV-Vis spectrometer (Shimadzu UV-1800 at λmax = 465 nm). The pH of the solutions was measured by a pH meter (Rowescience WP-90Z). Whatman Filter Paper (No. 1) was used to separate the adsorbent from the aqueous solution. An electric blender (QASA QBL-1861A) was used to grind the adsorbent into fine particles. The groundnut shells were obtained from Obiaruku and Abraka as waste. All the chemicals used in this research were obtained from Jacio limited Warri Delta state, Nigeria.

Bio-adsorbent preparation

Groundnut shells were collected from Obiaruku and Abraka town (Delta state, Nigeria). Groundnut shell adsorbents were prepared as adopted from the work of [5]. Groundnut shells were rinsed with distilled water. After air-drying, they were cut into small pieces and placed in a ceramic pot. They were then heated in a muffle kiln at 60˚C for 2 hours. Lastly, the samples were grinded, and the groundnut shell adsorbent powders which passed through a 0.1 mm strainer were referred to as GSA.

Preparation of adsorbate

Methyl orange (MO) was prepared by weighing 1000 mg of methyl orange(MO), then it was added to the 1000 mL of distilled water in volumetric flask, this was stirred to obtain 1000 mg/L MO solution. This liquor was diluted to other different concentrations as required throughout the experiment.

Determination of adsorbent surface charge

The surface charge of the GSA otherwise called point of zero charge was investigated via the salt addition method [15, 16]. 0.1mol/dm^3 of NaCl solution was prepared and 100mL of it was taken into various Erlenmeyer flasks and their pH were adjusted to the range of 2 to 12 using 0.1M HCl and NaOH respectively. The pH of the above setup was noted to be the initials designated as $pH_{1,}$ 0.5g of the GSA was added to each of the flask and agitated overnight using a shaker (wrist-Action shaker, Cole Parmer 51704 version) at 220rpm, the supernant were extracted separately after settling and the pH of each flask content were taken and noted to be finals (pH_2). A plot of ΔpH ($\Delta pH = pH_1 - pH_2$) vs pH_1 was made to obtain the pHpzc at the point of intercept at zero.

Determination of colour removal under varying conditions

Experimental procedure

Effect of pH

1.0g of the groundnut shell powder was weighed into five containers and 100 mL of the dye solution will be added to each container. The pH of these suspensions will be adjusted to 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0. The pH adjustment was made either by 0.5M HCl or 0.5M NaOH solution. The containers were tightly stopped, and the mixtures gently agitated on a rotary shaker for 50 minutes at room temperature and initial dye concentration of 50mg/L. At the end of the agitation time, the mixture was filtered through Whatman No.1 filter paper and the dye concentration of the filtrate will be determined using a UV/Visible Spectrophotometer.

Effect of contact time

1.0g of the groundnut shell powder was weighed into six plastic containers. The plastic containers containing the weighed adsorbent will be labeled appropriately for time intervals of 20, 40, 60, 80, 100 and 120 minutes. 100mL of the dye solution will be added to the container and shaken at room temperature set at pH 6 and dye concentration of 50mg/L. At the end of each time interval, the containers will be withdrawn, and the mixture will be filtered by through Whatman No.1 filter paper and the dye concentration of the filtrate will be determined using a UV/Visible Spectrophotometer.

Effect of initial dye concentration

1.0g of the groundnut shell powder was weighed into five plastic containers containing 100mL of 20, 40, 60, 80, 100 and 120 mg/L of methyl orange. The mixture will be shaken for 60 minutes using a rotary shaker at room temperature under pH 6. At the end of the given contact time, the mixture will be filtered through Whatman No.1 filter paper and the dye concentration of the filtrate will be determined using a UV/Visible Spectrophotometer.

Effect of dosage

0.2g, 0.4g, 0.6g, 0.8g, 1.0g and 1.2g of the adsorbent were added to 100 mL of the dye solution of 100mg/L in five containers. The mixtures will be shaken for 60minutes using rotary shaker at room temperature and pH 6. At the end of the given contact time, the mixture will be filtered through Whatman No.1 filter paper and the dye concentration of the filtrate will be determined using a UV/Visible Spectrophotometer.

Effect of temperature

1.0g of GSA was weighed into 100mL of 100mg/L of methyl orange dye in five separate flasks, this was agitated at 60rpm for 60 minutes at pH 6 in a rotatory thermostat water bath shaker (temperature controlled mechanical shaker (RATEK OM11 digital orbital shaking incubator) at 200 rpm). The supernant was taken by passing the mixture through a Whitman No. 1 filter paper, left to cool and the final methyl orange dye concentration was determined via UV/Visible spectrophotometer.

FTIR-ANALYSIS

The Fourier transform infra-red (FTIR) assessment was carried out on Groundnut Shell Adsorbent before and after adsorption process. This technique was used to determine the functional groups in the adsorbent which are responsible for adsorption of the dye. The FTIR was in the range 4000-400 cm^{-1} with resolution of 4 cm^{-1}. For this analysis, 0.30 g of the Groundnut Shell Adsorbent powder was encapsulated in 200 mg of KBr (sigma) [17]. The FTIR was recorded on a Fourier Transform Spectrometer at University of Lagos.

Data analysis

The adsorbed amounts (Q) of methyl orange by the groundnut shell and percentage removal efficiency (RE) at equilibrium will be estimated using equations (1) and (2) respectively.

Q = $(Co - Ce)V)/m$ - - - - - - (1)

% MO Removal =$(Co - Ce))/Co \times 100$ - - - - - (2)

Where C_o and C_e are the initial and equilibrium concentration of methyl orange respectively, V is the volume of solution and m is the mass of adsorbent used.

Equilibrium sorption and adsorption isotherms of dye removal

Sorption equilibria provide fundamental physico-chemical data for evaluating the applicability of physisorption processes as a unit operation usually described by isotherm models, whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature and pH. The sorption data will be tested against two adsorption isotherm models: Langmuir model and Freundlich model.

Pseudo-first order (Lagergren first order)

$\ln(qe - qt) = \ln qe - K_1 t$ - - - - - - (3)

Where, K_1 (min^{-1}) is the rate constant of the pseudo-first order relation, q(e) denotes the adsorption amount (mg g^{-1}). A plot of $\ln(qe - qt)$ vs t was made. K_1 is the slope while $lnqe$ is the vertical intercept

Pseudo-second order kinetic

$\frac{t}{q_t} = \frac{1}{k_2 q_e 2} + \frac{t}{q_e}$ - - - - - - - - - (4)

Where, k_2 (gmg^{-1} min^{-1}) is the rate constant of the Pseudo-second order relation, q(e)is the adsorption amount (mgg^{-1}). A plot of t/qt vs t was made, $1/qe$ is the slope and $\frac{1}{k_2 q_e 2}$ is the vertical intercept.

Langmuir Isotherm

Langmuir isotherm denotes a monolayer adsorption (Langmuir assumes that maximum adsorption occurs when the surface is covered by adsorbate) according to the mathematical relation given below.

$Ce/q\_e = 1/(K\_L\, q\mathrm{m}) + Ce/q\mathrm{m}$ - - - - - (5)

Where, qe is the amount of dye ion adsorbed per unit mass at equilibrium (mgg-^{1}), q_m is the maximum adsorbate that can be adsorbed per unit mass of adsorbent (mgg^{-1}), kL is (Langmuir constant) the adsorption equilibrium constant and Ce is the concentration of adsorbate (mgL^{-1}). A plot of $Ce/q\mathrm{e}$ against Ce was made to derive values for the constant.

The basic assumption is that there is a formation of a monolayer of the adsorbate on the outer surface of the adsorbent and after that, no further adsorption takes place. It allows the calculation of adsorption capacities and the Langmuir constants where the characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor RL)which describes the types of isotherms and is defined by:

$RL = 1/(1 + KL)\, Co)$ - -- - - - - (6)

Where, R_L is a dimensionless separation factor, Co is methy orange dye concentraction in mgL^{-1} and K$_L$ is Langmuir constant. R_L indicates the shape of the isotherm accordingly.

Table 1: Dimensionless separation factor R$_L$ and types of isotherm

Value of R$_L$	Type of isotherm
$R_L > 1$	Unfavourable
$R_{L\,=}\,1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Source; [18]

Freundlich Isotherm determination

This model is most applicable with heterogeneous surface adsorption process [5, 19, 20]. It also gives the details of surface heterogeneity, adsorption intensity and capacity respectively.

The linearized isothermal model can be expressed as below.

$\log q\_e = \log Kf + 1/n\, log Ce$ - - - - - - (7)

Where:

$qe$is adsorption at equilibrium, Ce is concentration of adsorbate in solution at equilibrium. Kf = capacity of adsorption, $1/n$ intensity of adsorption [19]. $Kf$and$1/n$ can be obtained from the linear plot of logqe vs log Ce and the slope and intercept extrapolated which corresponds to $1/n$ and Kf respectively

Adsorption Thermodynamics

In determining the enthalpy, entropy and Gibb's free energy, the following mathematical equations were applied.

$\Delta G = \Delta H - T\Delta S$ (Gibbs free energy) - - - - - - (8)

$\ln KGSA = \Delta S/R - \Delta H/RT$ (Vant Hoff) - - - - - (9)

$\Delta G = -RTln \ln K\_GSA$ (Arrhenius) - - - - - - (10)

$\ln(1 - \Theta) = S^{\wedge} * + Ea/(RT)$(Clausius-Clapeyron model) - - (11)

Where;

$KGSA =$ Adsorption equilibrium constant for groundnut shell adsorbent, $\Delta S =$ Entropychange (JK^{-1}mol^{-1}), $\Delta G =$ Gibbs free energy (kJmol^{-1}), ΔH = Enthalpy (kJmol^{-1}), $T =$ Temperature (K), Ea = Activation energy (kJmol^{-1}). Θ = Surface area coverage (mg/L), $S *$=Sticking probability, $R =$ Molar gas constant (Jmol^{-1}K^{-1})

A graph of $\ln k$ was plotted against $1/\mathrm{T}$ and in (1-Θ) Vs 1/T, the slope and intercept, ΔH, S*, Ea and ΔS were calculated respectively.

3.0 RESULTS AND DISCUSSION

3.1 Surface charge

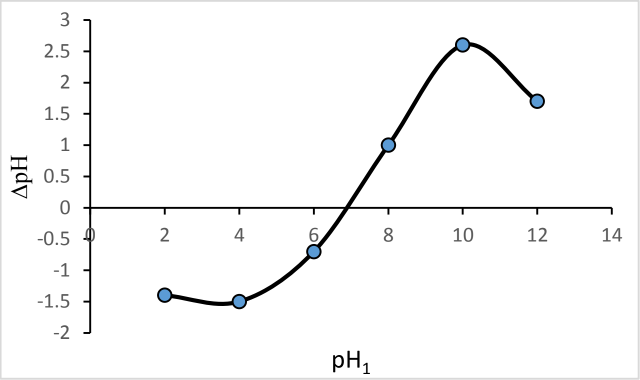

Fig 1: pHpzc plot for methyl orange adsorption using groundnut shell Adsorbent

From Fig 1 above, the pH at point of zero charge is 6.8, by implication, the adsorbent can assume positive charged surface at pH below the pHpzc while it will be negative at pH above the pHpzc [16, 15]. Similar value of 6.7 was reported by [16] while [15] reported acidic value of 5.4 and negative surface charge of 9.56.

Fourier Transform Infrared (FTIR)

The observed bands and interpretations are summarized in table 2 below**.**

Table 2: Summary of observations from FTIR spectrum

Observed bands before adsorption (cm^{-1})	Observed bands after adsorption (cm^{-1})	Remark	Similar observations made
3490.2	3384	O – H stretching	[22] [23]
2954	2561	C – H stretching of alkane and aldehyde group	[24] [21]
2034	2016.7	Weak C – O vibration	
1630		C = O stretching due to hemicellulose, lignin or cellulose	
1528.6	1528	Ring/aromatic vibration	
1450	1459	-CH$_2$ bending vibration	
1602	-	C = C stretching	
1120	1032	Strong C – O due to cellulose	
1031		C – C, C – O, C – O – C, vibration due to cellulose, Hemicelluloses, and lignin	
886.7		C – H deformation linked with glucose ring	

The major bands mostly functional groups of celluloses, hemicelluloses, and lignin. The result also revealed that groundnut shell has a lot of functional active sites suitable for adsorption [21]

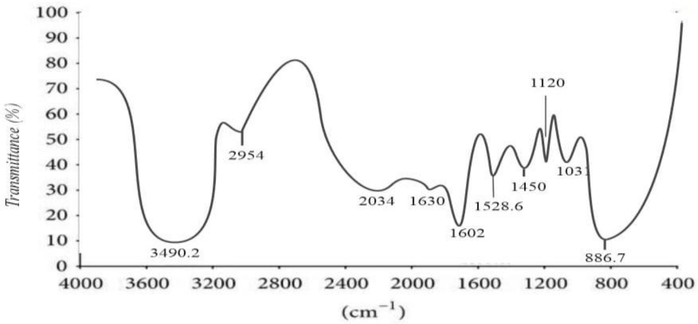

Fig 2a: FTIR spectrum of groundnut shell Adsorbent before adsorption process.

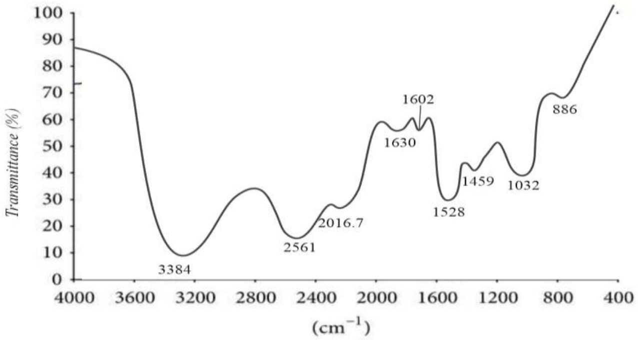

Fig 2b: FTIR spectrum of groundnut shell Adsorbent after adsorption process

Proximate Analysis.

The analysis was done as described by [17] in [25]

Adsorption Parameters Studies

Effect of Initial concentration

Table 3: Values for dependence of adsorption efficiency/capacity on initial concentration.

Initial Conc (g/dm^3)	MO Removal Efficiency (%)	$q_e$mg/g)
20	42	4.2
40	55.6	5.56
60	59.8	5.98
80	61	6.1
100	72	7.2
120	60	6

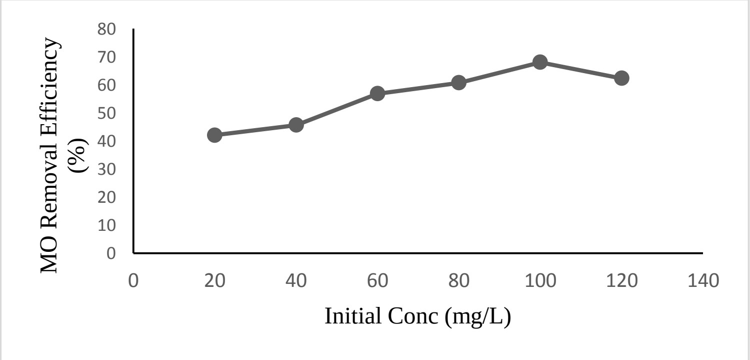

Fig 3: Plot of Methyl Orange Removal Efficiency (%) Vs Initial Conc (g/dm^3)

Initial dye concentration can affect the removal of MO either by increasing or decreasing the possible binding sites availability. From fig 4 MO Removal Efficiency (%) increased from 42 to 68% with the adsorption capacity of 4.2 to 7.2mg/g before a decline was observed. This observed increase in adsorption efficiency as initial concentration increases may be because of more adsorbate (methyl orange) molecules by the active sites of the adsorbent (groundnut shell). The optimum initial concentration of methyl orange in this study was observed as 100mg/l with the efficiency 68% and 7.2mg/g similar observation was made by [26] were adsorption increase with increase in initial dye concentration, [27] also reported 100mg/l in the adsorption of malachite green dye on groundnut shell activated carbon, similar view was also reported by [29] however [29 and 30] reported a conflicting observation of decrease in adsorption with decrease in initial dye concentration.

Effect of pH

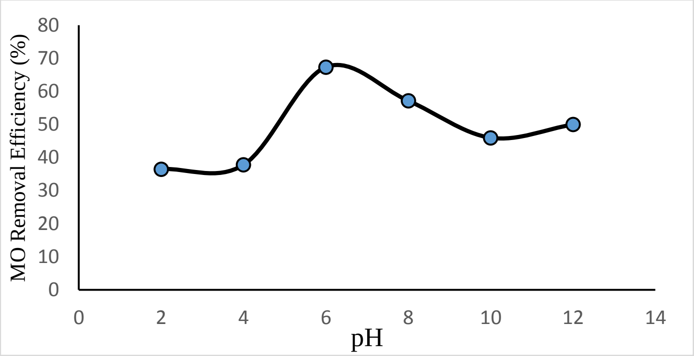

Fig 4: Plot of Methyl Orange Removal Efficiency (%) Vs pH

The plot shown in fig 4 revealed that the MO Removal Efficiency (%) adsorbent increases with increase in pH from 36.53 - 67.38 in respect of pH 2 – 6 before a decline was observed. The optimum pH the GSA adsorption efficacy is 6.0 with adsorption capacity of 6.74 mg/g. similar view of 6.68 was upheld by [31] when carbonized groundnut shell was deployed for the abatement of methylene blue dye from aqueous solution. However, this result conflicts with the pH 8 and 10 reported by [32] in the adsorption of crystal violet and methylene blue dyes respectively. The increase in MO Removal Efficiency (%) maybe due to higher ionization resulting to the presence of more positive charges which upheld the negative ions of the adsorbate (methyl orange), this was affirmed by the pHpzc value of 6.8, adsorption processes below such value, the adsorbent assumed a positive charge [33].Table 2 values for dependence of adsorption efficiency/capacity on pH.

Effects of Adsorbent Dosage on adsorption of Methyl Orange (MO)

From the fig 5 the MO Removal Efficiency (%) increases as the dosage increases to the range of 45.1 to 70.5 in respect of 0.2 to 1.0 dosages before a declined was observed. Therefore, the optimum dosage was recorded at 1.0g with efficiency of 70.5 % and 6.95 mg/g absorption capacity. The observed increased in removal efficiency can be ascribed to the availability of more absorbent active sites for the uptake of the absorbate molecules [21] similar observation of 1g dosage of absorbent was made by [34] in the removal of dichlorovos using groundnut shell. [31 and 21] posited the dosage of 1g and 2g respectively using groundnut shell as absorbent.

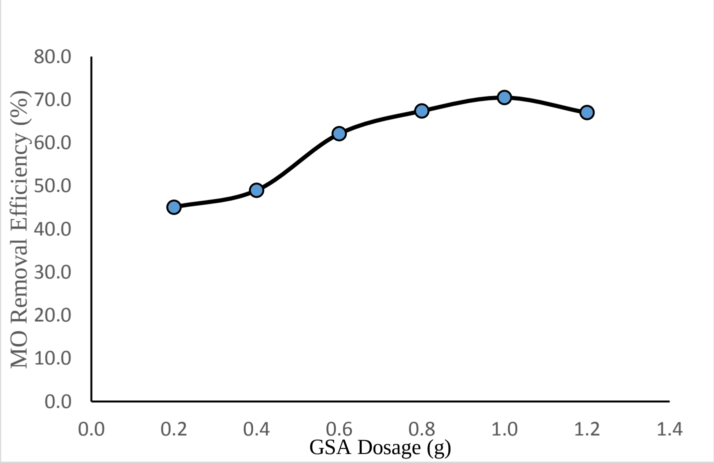

Fig 5: Plot of Methyl Orange Removal Efficiency (%) Vs groundnut shell Dosage (g)

Table 4: Values for dependence of adsorption efficiency/capacity on GSA Dosage (g).

GSA Dosage (g)	MO Removal Efficiency (%)	q_e (mg/g)
0.2	45.1	4.51
0.4	49.0	4.9
0.6	62.1	6.21
0.8	67.4	6.74
1.0	69.5	6.95
1.2	67.0	6.7

Effects of Temperature

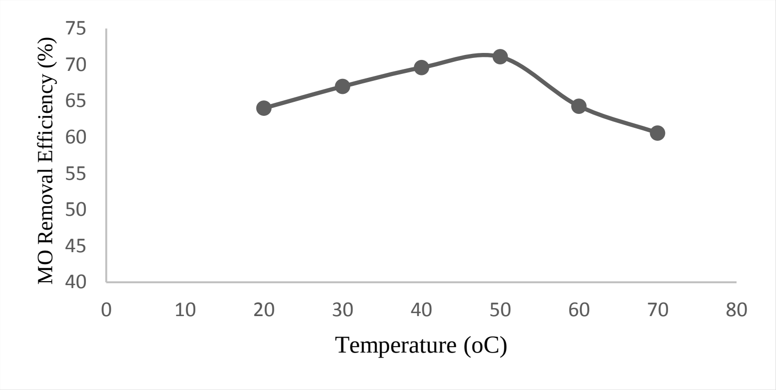

Fig 6: Plot of Methyl orange Removal Efficiency (%) Vs Temperature (°C)

The rate of dye molecules diffusion is a temperature control process hence alteration of the temperature affects the equilibrium capacity of GSA for the dye (MO), therefore increase in temperature result to fast diffusion of dye molecules through the boundary layer and the pores of GSA leading to lower resistance put up by viscous force by liquid phase. This increase in adsorption efficiency of GSA may be ascribed to enlargement of pore size [35]. Fig 7 showed increase in adsorption efficiency of methyl orange by GSA from 64 to 71.1% (6.4 to 7.11mg/g) as temperature increased from 20 to 50 °C hence the optimum temperature is 50°C. A close view to this result was reported by [35 and 21].

Effect of Contact Time

Impact of contact Time on the Adsorption of Methyl orange dye by groundnut shell

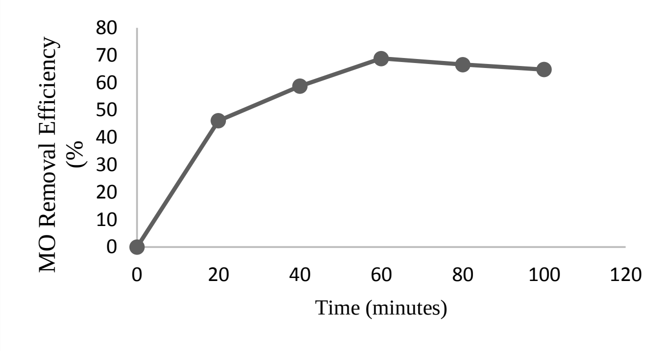

Fig 7: Plot of Methyl Orange Removal Efficiency (%) Vs Contact Time (mins)

The impact of contact time on the adsorption of MO by GSA was investigated under the variation of time at a range of 20 to 100 minutes and the result was visualized in fig 6. From the plot, the MO removal efficiency increased rapidly from 46.1 – 68.8% with adsorption capacity of 4.61 to 6.88 mg/g before falling sharply, further increased in contact time reflects no significant change in equilibrium concentration, this showed that adsorption process of MO attained equilibrium at time 60 minutes as the optimal point. The diffusion or migration of MO dye molecules take time to pass through the adsorbent pores and boundary, hence the observed rapid increase in the adsorption capacity or rate with time, after the equilibrium, a decline was observed, this maybe as a result of adsorbent surface-active site saturation with the dye molecules this means the available active sites of the adsorbent might have been covered by dye molecules. This result is in consonance with that of [36, 37] as well as [38] all reported the same 60 minutes using various biosorbent respectively, in opposition this result, [27] reported 30 minutes for the adsorption of malachite green dye using groundnut shell adsorbent, also [35] and [38] reported 70 and 90 minutes respectively.

Methyl orange Adsorption Kinetics.

The adsorption kinetics was investigated under variable time of 20 – 100 minutes, and the result were subjected to two kinetic model (Pseudo first order and Pseudo second order models) as presented in Fig. 8 and Fig. 9 below,

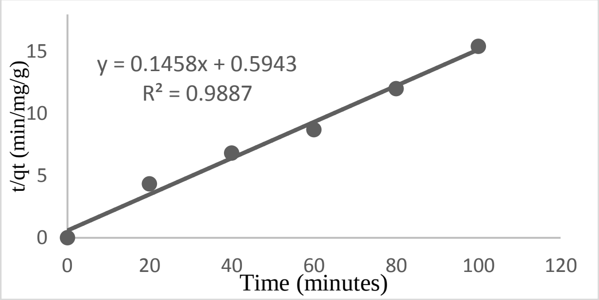

Fig 8: Pseudo second order plot of the Adsorption of Methyl Orange unto groundnut shell (pH 2-12, Time 20-100, Temperature 20-70, Dosage 0.2-1.2, Initial Concentration 20-120)

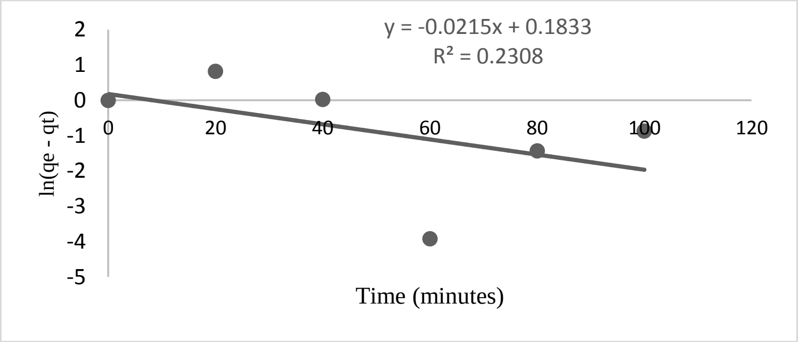

Fig 9: Plot of Pseudo- first order plot of the Adsorption of Methyl Orange unto groundnut shell (pH 2-12, Time 20-100, Temperature 20-70, Dosage 0.2-1.2, Initial Concentration 20-120)

The value for the regression coefficient (R^2) of 0.2308 was for two as shown in Fig 9 hence it was concluded that the result did not fit pseudo first order model and no further evaluations were made, however, the values of the coefficient of correlation for the pseudo second order kinetic model were higher than that of the pseudo-first order model. This implies that the pseudo-second order kinetic model for the experiment data is better fit than the pseudo-first order model, pseudo second order kinetic is an indication that ions were exchanged in the adsorption process [39]. This result agreed with that of [40, 4, 41, and 31] where groundnut shell was used in different status to adsorbed various dyes from aqueous solutions and all fitted pseudo second order model better.

For the pseudo-second order kinetic model, the experimental adsorption capacity value of 6.88 mg g^{-1} is very close to those of the calculated adsorption capacity value of 6.86 mg g^{-1} as shown in Table 5.

Table 5: Values for Pseudo second order kinetic

q_e (mg g^{-1}) cal	q_e (mg g^{-1}) Exp	h (mg g^{-1} min^{-1})	K_2 (g mg^{-1} min^{-1})	R^2
6.86	6.88	1.683	0.0358	0.9887

This observed adsorption capacity is higher than that 2.617 mg g^{-1} of [42] as well as 4.83 mg g^{-1} of [37] which implies that groundnut shell adsorbed dye molecules from aqueous solution than adsorption of chromium from tannery wastewater.

Adsorption Isotherm

The Langmuir and Freundlich isotherms were applied to the adsorption data generated and the plots are presented in Fig. 10 and 11 below. The values of the constants obtained when experimental data for the methyl orange dye adsorption were fitted to Langmuir and Freundlich isotherm models are shown in Table 6 and 7

Table 6: Values for Langmuir isotherm constants for the adsorption of methyl orange onto GSA

q_m	K_L	R_L	R^2
2.96	0.051	0.16	0.9763

Table 7: Values for Freundlich isotherm constants for the adsorption of methyl orange onto GSA

1/n	N	K_f (L/mg)
20.7695	1.2995	7.402

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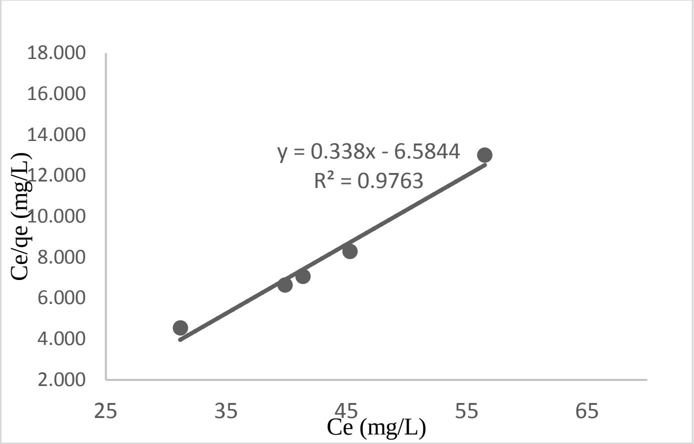

Fig. 10: Langmuir Isotherm plot for the adsorption of methyl orange dye onto groundnut shell.

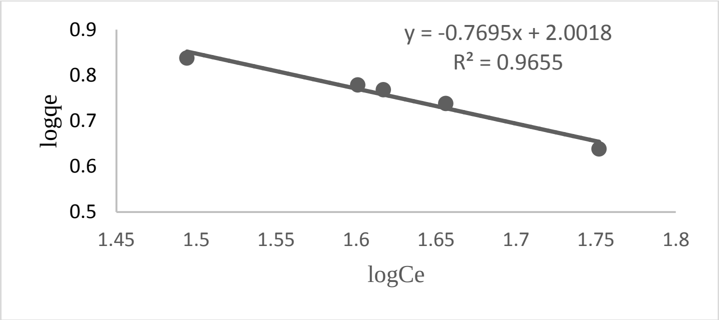

Fig. 11: Freundlich Isotherm plot for the adsorption of methyl orange dye onto groundnut shell.

The plot in fig. 10 above revealed a good fit of the experimental data on Langmuir isotherm with the regression coefficient of 0.9763. This implies that the adsorption process was dominated by monolayer surface formation, and it may be formed through diffusion of molecules, that is, its non-ideal for the development non-uniform multilayer [28]. The separation factor and other Langmuir constants are calculated and presented in table below. Table 6 Values for Langmuir isotherm constants for the adsorption of methyl orange onto GSA. The maximum adsorption capacity was observed to be 2.96; this showed a good capacity though lower than some reported data in literature [21, 27 and 43]. The separation factor R_L is less than 1 ($R_L < 1$) which means the adsorption was favourable [15].

Freundlich Isotherm Determination

This model is most applicable with heterogeneous surface adsorption process [5, 19], it also gives the details of surface heterogeneity, adsoption intensity and capacity respectively.

The linearized isothermal model is given as.
$$\text{Log}qe = \log Kf \;+\; 1/n\, logCe \qquad (12)$$
Where:
$qe$is adsorption at equilibrium, Ce is concentration of adsorbate in solution at equilibrium. Kf = capacity of adsorption, $1/n$ intensity of adsorption [19].Kf and $1/n$ can be obtained from the linear plot of $\log q_e$ vs log Ce and the slope and intercept extrapolated which corresponds to $1/n$ and Kf respectively.

From Fig.11 the experimental data also fit Freundlich model which implies that heterogenous surface site energy distribution might took place [18], the model constants were also calculated as presented in Table 4. Table 7. Values for Freundlich isotherm constants for the adsorption of methyl orange onto GSA. The Freundlich adsorption capacity of GSA (K_f L/mg) was found to be 7.402, which indicates a good surface adsorption capacity. The adsorption intensity (1/n) from table 4.4above showed 0.7695 which is less than 1 ($1/n < 1$) pointing to a non- cooperating adsorption process, meaning it maybe through physical either by diffusion holding by Van der Waal force [25]. The value for n (1.2995) is greater than 1 ($n > 1$) reflecting physical adsorption process because of surface-active sites distribution [28, 39, 36].

The Langmuir isotherm was used to test the experimental data for the removal of methyl orange dye using the groundnut shell adsorbent. The values for the constants are given in Tables 6 and 7. The values of the correlation coefficient showed that the uptake methyl orange from aqueous solution can be described by Langmuir isotherm. The values of the constants for the Freundlich isotherm are displayed in Tables 7. The R^2 values showed that the adsorption of methyl orange dye can be approximated with the Freundlich isotherm. However, the best fit was obtained using the Langmuir isotherm.

Thermodynamics Studies.

To ascertain the feasibility, spontaneity and mechanism of the adsorption process, the experimental result under the effect of temperature was subjected to thermodynamics analysis using Vant Hoff and Clausius-Clapeyron models with the plots of $\ln K_{GSA}$ Vs 1/T and ln(1-Ɵ) Vs 1/T respectively [44], the plots are presented in Fig 12 and Fig 13 below and the various thermodynamic parameters derived from the plot are presented in Table 8.

Table 8: Values for thermodynamics parameters

T(K)	ΔG KJ/Mol	ΔH KJ/Mol	ΔS J/Mol	Ea KJ/Mol	n	S*	Ɵ	R^2 (Clausius)	R^2 (Vant
293		-8.65	34.345	5.85		-3.43		0.9923	0.99
	-1.4016				1.8		0.640		
303	-1.7840				2.0		0.670		
313	-2.1555				2.3		0.696		
323	-2.4175				2.5		0.711		

The regression coefficient value for both plots showed a fit of the data to the two thermodynamics models. The free energy change (ΔG) obtained is negative which is a pointer of feasible and spontaneous adsorption process [35] and the value decreased and higher temperature, this means the process was not favorable at higher temperature therefore, the process is assumed to be physisorption. Negative value of enthalpy change (ΔH) indicated an exothermic adsorption process hence, no additional energy is needed to start up the process and it is less than 40 KJ/Mol, this buttressed the physisorption claim. The sticking factor (S*) obtained from Clausius-Clapeyron plot was less than 1 hence the methyl orange dye molecules do not sticked permanently to the groundnut shell adsorbent therefore it can be desorbed easily. Activation energy value derived is 5.85kj/mol which is in the range of physisorption values (< 40KJ/mol) [45, 46], it can be concluded that the process was a physisorption, similar view has been reported by [35, 39, 21, 26 and 29] respectively. The hopping number (n) which is the number of circles completed by dye molecule before binding to adsorbent site increased as temperature increased this was evident in the positive and large value of entropy change (ΔS) reflecting high rate of disorderliness, this result to increase in the fraction of GSA surface covered by methyl orange molecules (Ɵ) as temperature increased.

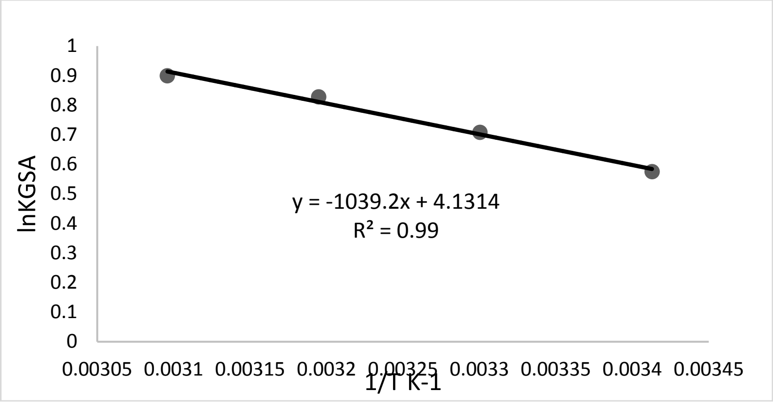

Fig.12: Vant Hoff plot of lnK against 1/T (K-1) for the adsorption of methyl orange onto Groundnut Shell Adsorbent.

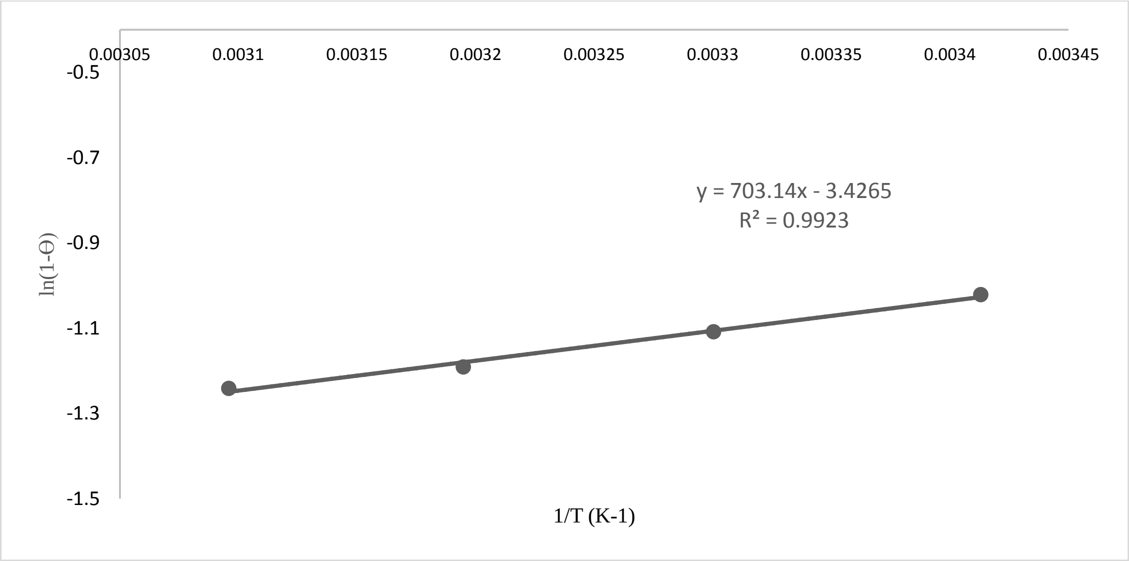

Fig.13: Clausius-Clapeyron plot of ln(1-ϴ) against 1/T (K-1) for the adsorption of methyl orange onto Groundnut Shell Adsorbent

4.0 CONCLUSION

From the experimental observation, results, and discussion of this research work, it can be inferred that: groundnut shell is a cheap, and good alternative source of adsorbing dye such as methyl orange from aqueous solution, The adsorption process is highly dependent on the pH, agitation time, adsorbent dose, adsorbate concentration,

The percentage removal and adsorption capacity of the adsorbent prepared from the groundnut shell adsorbent increased at a steady rate with acidic phase of pH.

The adsorption of the methyl orange followed a pseudo-second order kinetics mechanism; the adsorption of the dye is a monolayer sorption process as the best fit was obtained using the Langmuir Isotherm.

The FTIR spectra confirmed the presence of prominent peaks which confirmed the presence of –OH, -C-H, -C=O, -C-O, -C-C. These functional groups are responsible for the adsorption of the MO, The adsorption process is exothermic, spontaneous and a physisorption process as well as weak stickingness.

REFERENCES

[1] Chakraborty, P., Ramteke, D., Chakraborty S. and Nath B. N. (2014). Changes in metal contamination levels in estuarine sediments around India – An assessment. *Marine Pollution Bulletin,* 78: 15-25.

[2] Ikpeaiyeda, A. R. and Tesi, G. O. (2014). Sorption and Desorption Studies on Toxic Metals From Brewery Effluent Using Eggshell as Adsorbent. *Advances in Natural Science*, 7(2): 15-24.

[3] Renjith, K.R., Sudheesh, V., Shaji, A., George, E., Joseph, M.M., Ratheesh Kumar, C.S. and Chandramohana Kumar, N. (2015). Geochemical distribution, bioavailability and potential toxicity of some trace metals in a complex micro-tidal estuary, Southwest India.*Toxicological* and *Environmental Chemistry*, 98(1): 36-52.

[4] Ibrahim, M.B., Ibrahim, A.M., HAruna, M.A. and Yaro, M.S. (2013). Removal of congo red dye from aqueous solution using sugarcane baggase and Bambara groundnut shell. *Chemsearch Journal*, 4(1): 22-28

[5] Asiagwu, A.K., Emoyan, O.O. and Ojebah, C.K. (2018). Removal of tartrazine yellow dye from aqueous Solution using groundnut shell as biomass: Kinetic approach. *International Journal of Engineering Research and Technology*, 7(5): 404-411

[6] Alene, A.N., Abate, G.Y., Habte, A.T., (2020). Bioadsorption of Basic Blue Dye from Aqueous Solution onto Raw and Modified Waste Ash as Economical Alternative Bioadsorbent. *Journal of Chemistry* 11. https://doi.org/10.1155/2020/8746035.

[7] Metivier-Pignon, C., Faur, P. and Coirec, L. (2007). Adsorption of dyes onto activated carbon cloth using QSPRS as tools to approach adsorption mechanism. *Chemosphere*, 66: 887- 889

[8] Crini, G., Lichtfouse, E., Wilson, L.D., Morin-Crini, N., (2019). Conventional and non-conventional adsorbents for wastewater treatment. Environmental Chemistry Letters 17, 195–213. https://doi.org/10.1007/s10311-018-0786-8

[9] Imam, S.S. and Abdullahi, M. (2017). Adsorptive removal of methylene blue using groundnut shell activated carbon coated with Fe_2O_3. *IOSR Journal of Applied Chemistry*, 10(4): 12-21

[10] Das, N., Karthika, P., Vimala, R. and Vinodhini, V. (2008). Use of natural products as biosorbent of heavy metals—An overview. Natural Product Radiance, 7(2): 133 – 138.

[11] Kumar, S., Gunasekar, V. and Ponnusami, V. (2013). Removal of methylene blue from aqueous effluent using fixed bed of groundnut shell powder. *Journal of Chemistry*, Article ID 259819 https:// dx.doi.org/10.1155/2013/259819

[12] Jeyaseelan, C. and Chauchan, K. (2015). Removal of congo red from aqueous solution using groundnut shells. *Journal of Basic and Applied Engineering Research*, 2(11): 910-914

[13] Kamaraj, M. and Umamaheswari, P. (2017). Preparation and characterization of groundnut shell activated carbon as an efficient adsorbent for the removal of methylene blue dye from aqueous solution with microbiostatic activity. *Journal of Materials and Environmental Sciences*, 8(6): 2019-2025

[14] Kayranh, B., Gok, O., Gok, G. and Masutoglu, O.C. (2019). Textile dye removal from aqueous solution by using peanut and pistachio shells. *International Journal of Environmental Pollution and Environmental Modelling*, 2(5): 270-276

[15] Ezenwa, O.S and Ogochukwu, N.H. (2021). Comparative analysis and regenerative studies of alkaline modified groundnut shell as adsorbent for the removal of oil layer from polluted water. *Journal of engineering, research and report*, 20(2): 76 – 86.

[16] Boumehita, S., Lahrich, A., Benjelloun, Y., Lairini, S. Nevou, V and Zerouq, F. (2017). Application of peanut as a low-cost adsorbent for the removal of anionic dye from aqueous solutions. Journal of materials and environmental sciences 8(7): 2353 – 2364.

[17] AOAC, (2000). Official methods of analysis of Associaation of official chemists international, 17th Ed.

[18] Al-Ghouti, M.A. and Al-Absi, R.S. (2020). Mechanistic of the adsorption and thermodynamics aspect of cationic methylene blue dye on cellulosic olive stones biomass from wastewater. *Scientific Report*, 10, 15928. https://doi.org/10.1038/s41598-020-7299-3.

[19] Ayawei, N., Ebelegi, A.N., Wankasi, D., (2017). Modelling and Interpretation of Adsorption Isotherms. *Journal of Chemistry* 2017, 1–11. https://doi.org/10.1155/2017/3039817

[20] Ademoriyo, C.O., and Enyoh, C.E. (2020). Batch adsorption study of sunset yellow and tartrazine using coconut and groundnut shells. Journal of biomedical research and environmental sciences. 6(9): 163 – 172. http://doi.org/10.37871/jbres1137.

[21] Bayou, J., Pelig-Ba, K.B and Abukari, M.A. (2019). Adsorptive removal of chromium from aqueous solution onto groundnut shell. Applied water science, 9(107): 2-11. https://doi.org/10.1007/s13201-019-09-8

[22] Wu, J., Xia, A., Chen, C., Feng, L., Su, X., and Wang, X. (2020). adsorption thermodynamic and dynamics of three typical dyes onto bioadsorbent , spent substrate of pleurotus eryngii. *International journal of environment, research, and public health*. 16(5): 679. https//doi.org/10.3390/IJERPH/6050679.

[23] Ajala, L.O and Ali, F.E. (2020). Preparation and characterization of groundnut shell-based activated charcoal. *Journal of applied science and environmental management*, 24(12):2139 – 2146. https://dx.doi.org/10.4314/jasem.v24i12.20

[24] Etim, E.U. (2019). Removal of methylene blue from aqueous solution by adsorption onto groundnut waste. *Biomed journal of science and technological research*. 15(3). https://doi.org/10.26717/BJSTR.2019.002701

[25] Duc, P.A., Dharanipaya, P., Velmuruyari, B.K and Shamugavadivu, M. (2019). Groundnut shell: a beneficial bio-waste. *Biocatalysis and Agricultural Biotechnology*. 20: 101200.

[26] Vijayakumar, G., Tamilarasan, R and Dharmendirakumar. M. (2012). Adsorption kinetic, equilibrium and thermodynamics studies on the removal of basic dye rhodamine – B from aqueous solution by the use of natural adsorbent perlite. *Journal of material and environmental science*s, 3(1): 157 – 170.

[27] Malik, R and Wate, S.R. (2007). Adsorption of malachite green on groundnut shell waste-based powder activated carbon, waste management, 27(9): 1129-1138. https://doi.org/10.1016/j.wasman.2006.06.009.

[28] Terangpi, P and Chakraborty, S. (2007). Adsorption kinetic and equilibrium studies of the removal of acid azo dye by aniline formaldehyde condensate. *Applied Water Sciences*, 7(7): 3661 – 3671.

[29] Zehra, T., Piryantha, N., and Lim, L. (2016). Removal of crystal violet dye from aqueous solution using yeast treated peat as adsorbent: thermodynamics, kinetic and equilibrium studies. *Environmental and earth sciences*, 75(357).

[30] Hameed, B. and El-Khaiary, M., (2008). Sorption kinetics and isotherm studies of a cationic dye using agricultural waste: broad bean peels. *Journal of Hazardous Materials*, 154(1): 639-648

[31] Ungwanen, J.A., Iorav, H.N and Okpanachi, J. (2019). Kinetic and equilibrium studies of the adsorption of methylene blue dye from aqueous solution on carbonized groundnut shell. FUPRE Journal of scientific and Industrial research, 3(3): 52-65.

[32] Zango, Z.U and Imam, S.S. (2018). Evaluation of microcrystalline cellulose from groundnut shell for the removal of crystal violet and methylene blue. Nanoscience and Nanotechnology, 8(1): 1-6. https://doi.org/10.5923/j.nn.20180801.01.

[33] Gimba, C.E., Salihu, A.A., Kagba, J.A., Turoti, M., Itodo, A.U and Sarigya, A.I, (2010). Study of pesticide (Dichlorovos) removal from aqueous medium by *arachis hypogea* (Groundnut) shell using GC/MS. *World rural Observation*, 2(1): 1-9

[34] Banerjee, S., and Chattopadyaya, M. C. (2013). Adsorption characteristics for the removal of toxic dye, tartrazine from aqueous solution by low-cost agricultural by-products. *Arabian Journal of Chemistry*, 10(2); 31629 – 31638. https://doi.org/10.106/j.arabjc.2013.06.005.

[35] Desta, M.B. (2013). Langmuir and Freundlich isotherm studies for adsorption of textile metal ions onto Teff straw (Eragrotis tef) agricultural waste. *Journal of thermodynamics*. 2013. https://doi.org/10.1155/2013/375830

[36] Hidayat, P., Dikma, D.N., Putra, A., Chafidz, A., Zulkania, A and Astuti, W. (2021). Effect of pH and contact time on the adsorption of Pb(ii) by Kapok wood (ceiba pentandra) sawdust-based adsorbent. *Material science forum*, 1029: 159 – 165. https://doi.org/10.4028/www.scientific.net/msf.1029.159

[37] Kurniawati, D., Bahrizal, T.K., Adella, F. and Salmariza, S. (2021). Effect of contact time on adsorption of Rhodamine – B, Methyl orange and methylene blue colours on langsat shell with batch methods. *Journal of Physics: conference series*. 1788012008.

[38] Benjelloun, M., Miyah, Y., Evrendilik, G.A., Zerouq, F and Lairan, S. (2021). Recent advances in kinetic models, their application on dye types. *Arabian Journal of Chemistry*, 14 (103031). https://doi.org/10.1016/j.arabjc.2021.103031.

[39] Asiagwu A. K. (2018). "Removal of tartrazine yellow dye from aqueous solution using groundnut shell as biomass: kinetic approach*," International Journal of Engineering Research*, 7(5): 156-178.

[40] Trividal, N.S., Kharkhar, R.A. and Mandevgane, S.A. (2016). 2,4 – Dichlorophenoxyacetic acid adsorption on adsorbent prepared from groundnut shell: effect of preparation conditions on equilibrium adsorption capacity. Arabian Journal of Chemistry. 12: 4541-4549.

[41] Mwegoha, W.J.S and Lema, M.W.J. (2016). Effectiveness of activated groundnut shell to remove chromium from tannery wastewater. *International journal of environmental monitoring and protection*, 3(4): 36 – 42.

[42] Sachdev, D., Shrivastava, H., Sharma, K.S., Srivastava, S., Tadipalli, S., Bhullar., N.K and Shahu, O.P (2022). Potentials for hydrothermally separated groundnut shell fibres for the removal of methylene blue dye. Materials today: proceedings, 48(5): 1559 – 1568. https://doi.org/10/1016/j.matpr.2021.09.466

[43] Morais, L.C., Freitas, M. O., Gonealves, E, P., Vasconeclos, L.T. and Beca, C.G.G. (1999). Reactive removal from wastewater by adsorption on eucalyptus bark, variables that define the process. Water Research. 33: 979-988.

[44] Nwosu, F.O., Olu-Owolabi, B.I and Adebowale, K.O. (2012). Kinetic and thermodynamics adsorption of Pb(ii) abd Cd(ii) ions from used oil ontotheretia nerifolia nutshell active carbon. 15(2): 225-252.