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Adsorption of methylene blue onto Modified Agricultural Waste

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Abstract

Waste water discharged from industries contains dyes which prove danger to the ecology, affecting aquatic habitat and humans, due to that, different techniques on waste water treatment have been used throughout the years among which adsorption process triumphed, and this is due to low cost, high efficiency and controlled end product. The aim of this work is to study the efficiency of modified kolanut pod (MKP) to adsorb methylene blue (MB) from aqueous solution. A batch process was carried out to study by optimizing, the effect of parameters such as contact time (10min to 180min), initial concentration (5mg/l to 150mg/l), adsorbent dosage (0.2g to 1g), temperature (303k to 333k), and pH (3 to 11). Characterization of the adsorbent was carried out using Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM), the results obtained showed a difference in the micrograph obtained before and after adsorption while the shifting and disappearance of peaks where also observed in the FTIR spectra respectively . Five isothermal models; the Langmuir, Freundlich, Dubinin-Radushkevich, Tempkin and Hasley were used to describe the adsorption process of which the data obtained best fit Freundlich and Hasley models. The kinetic studies revealed that adsorption of MB on to MKP follows pseudo second-order. The thermodynamic parameters obtained was a negative change in Gibbs Free energy which indicate spontaneity of the system, a positive change in Entropy which indicate a higher degree in randomness, and a high change in Enthalpy which suggest chemisorption. The collective results suggest MKP can be employed as a potential adsorbent for the removal of MB with 94% removal.

Keywords: *Colanut pod; Methylene blue; Adsorption; Chemsorption; Isotherm.*

1. Introduction

Nearly one-seventh of the world rivers are been affected by rigorous organic pollution, these rivers stretches to Africa, Asia and Latin America, this have been increasing steadily for years [1]. An estimation have been suggested the amount of waste water released from industries will double by 2025[2]. Monitoring the sources of wastewater under industry its known that: Textile manufacturing industries is confirmed to be one of the largest industries that produces wastewater, and have a characteristics of a strong color, highly pH fluctuation, chemical oxygen high demand (COD), and the biotoxicity [3], in fact, the real hazards caused by these colored and solid wastes in water is ruled as often toxic, carcinogenic, mutagenic or even explosive that might affect aquatic biota and also humans [4-6]. water exposed to organic dyes that includes methylene blue, end up with to a lot of diseases and numerous health problems. Methylene blue, MB, is one of the most used synthetic dyes known for its promising yield in cotton, wood, and silk dying [7]. Therefore, the treatment of these harmful dye effluents is emergency needed due to the negative impacts it result to [7]. Currently, numerous processes for treatment of effluents discharged from industries containing dyes is available, amongst which biodegradation can be mentioned [8], also chemical oxidation [9], foam flotation [9], electrolysis [10], adsorption [11], electro-coagulation [12] and photocatalysis [13] are used, among which, adsorption process is known to be the most suitable method due to its high efficiency and economic consideration [14]. In recent years, there has been growing interest in finding inexpensive and effective synthetic and natural adsorbents, or their modified products [15]. Chemically modifying of adsorbent have been efficient in the recent years and it was reported by [16] whom used chemically treated kola nut pod as low-cost natural adsorbent for the removal of 2,4 dinitrophenol from synthetic wastewater. Also Maryam [15] compared adsorption ability of treated sawdust for removal of Basic Red 46 and Reactive Red 196 as models of cationic and anionic dyes, respectively which result to an optimum percentage removal of 99.72 and 98.82, also Yemei [17] reported to have used an anionic adsorbent prepared by the means of grafting a citrate onto pomelo peel (PPL) to adsorb methylene blue (MB) from aqueous solution both the PPL and the modified pomelo peel (MPPL) yield good amount of adsorption capacity of which the MPPL's was higher than the PPL with 117.5mg/g.

Table 1. some characteristics of the research dyes. [21]

Characteristics	**MB**
General name	Methylene Blue
Chemical formula	$C_{16}H_{18}N_3ClS$
IUPAC name	3,7-bis(Dimethylamino)-Phenazathioniumchloride, Tetramethylthioninechloride, Trihydrate
Molecular weight	373.9 g/mol
Melting point	100 – 110°C
Physical state and form	Solid and powdered
Water solubility at	At 20°C 40 g/L
Bulk density	400-600Kgm^{-3}
Type of dye	Basic dye Cationic

Kola-nut is a tree crop found in the tropics, with more than 20 different species, Kola nitida (Gbanja) and Kola acumulata (Abata) are the two main species grown in Nigeria [18], a good quantity of kola is exported to other African

countries and Europe as well as North America [19]. Olubgenga [20] reported using it as adsorbent, it was also chemically treated and used as adsorbent as reported by Samuel [16]. Methylene blue been the dye in the present work has a wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools, some of it characteristics are been mentioned in table 1 below. The aim of the present work is to test the efficiency of MKP as an adsorbent in the removal of MB from aqueous solution.

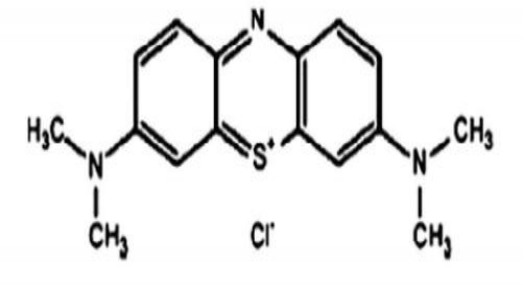

Figure 1. Chemical structure of methylene blue [21]

2. Materials and methods

2.1 *Sample collection*

Approximately, 100 kolanut pods and its content was obtained from a village called Ikoromoja in Atakunmosa east local government area of Osun state, south western Nigeria.

Figure 2. *Kola nitida*

2.2. *Sample preparation*

The kolanut pod was cracked open and its content emptied so as to use the kolanut pod, the kolanut pod were chopped in to smaller pieces to facilitate the drying process and the debris were washed thoroughly due to high viscos liquid that it produces. The rinsing of the samples were carried out with deionized water and air dried for two weeks and was subsequently washed severally with deionized water to remove all the viscos substance and finally air dried, labelled and stored for further usage.[16] with little modification

2.3. Preparation of chemically modified Kolanut Pod

A solution of HCl (10M) was used to activate surface sites of kolanut pod and remove tanning compounds which can interfere with the treated effluent. Several studies showed that HCl serves as a more effective treatment reagent

compared to other strong acids such as H2SO4 and HNO3, bases, and alcohols [22-23]. Exactly 7 g of dried kolanut pod was introduced into 100 mL of 10 M HCl solution in 10 pieces of Erlenmeyer conical flask and shake with an electrical shaker, at 60oC for 1 h 15minutes. It was then washed severally with deionized water to attain a neutral pH and then dried at 60oC for 24 h. Finally, the dried material was ground and sieved to get the particle size of 0.5mm mesh size and then kept in a plastic container labelled MKP. The procedure was adopted from Maryam [15] with slight modifications.

2.4. Adsorbate preparation

A stock solution of MB was prepared by dissolving 1g of the dye in 1L of distilled water. Experimental solutions of the desired concentrations were obtained by dilutions from these stock solutions thereafter to produce 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20mg/L for calibration curve and 10mg/L for adsorption studies.

2.5 characterization and analysis

The various functional group present on the MKP surface were determined using Fourier Transform Infrared Analysis (FTIR). The concentration of dyes in the solution was measured by PerkinElmer UV-visible spectrophotometer at the maximum wavelength (i.e. 606nm for MB). The surface morphology was revealed through the use of scanning electron microscope (SEM) model at 2000 magnification.

2.6 batch adsorption experiment

The batch adsorption process was carried out in a 120ml stopped bottle containing 50 mL of 10 mg/L MB. 0.2 g of MKP was added in the solution and then agitated using an electric agitator at 200rpm for 180 min at ambient temperature (31.5) samples were taken out after intervals of 10, 20, 30, 60, 90, 120, 150, 180min and then filtered, after which concentrations were determined using PerkinElmer UV-spectrophotometer at an absorbance wavelength of 606nm. The optimized time parameter was achieved by calculating the highest percentage removal using equation (1) and highest adsorption capacity using equation (2)

$$\%removal = \frac{C_0 - C_t}{C_0} \text{X } 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \text{X } 100 \quad (2)$$

Where C0 (mg/L) is the initial dye concentration, Ce (mg/L) is the equilibrium dye concentration, m (g) is the sorbent mass, and V (L) is the volume of the dye solution. The remaining parameters were optimized by using the prior optimized parameters in the trend bellow.

- Initial concentration at intervals of (5, 10, 20, 30, 50, 70, 100, 120, 150ppm).
- Initial adsorbent dosage at intervals of (0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1g).
- Initial temperature at intervals of (30, 40, 50, 60^{o}C). [24]

3. Results and Discussions

3.1. surface chemistry

3.1.1. FT-IR spectroscopy

FT-IR spectroscopy was used to investigate the interactions between different species and changes in chemical compositions of the adsorbents before and after adsorption of the dyes. Figure 2 and 3 presents FTIR spectra of the adsorbent before and after adsorption of each dyes while Table 2 presents peaks and frequencies of IR absorption.

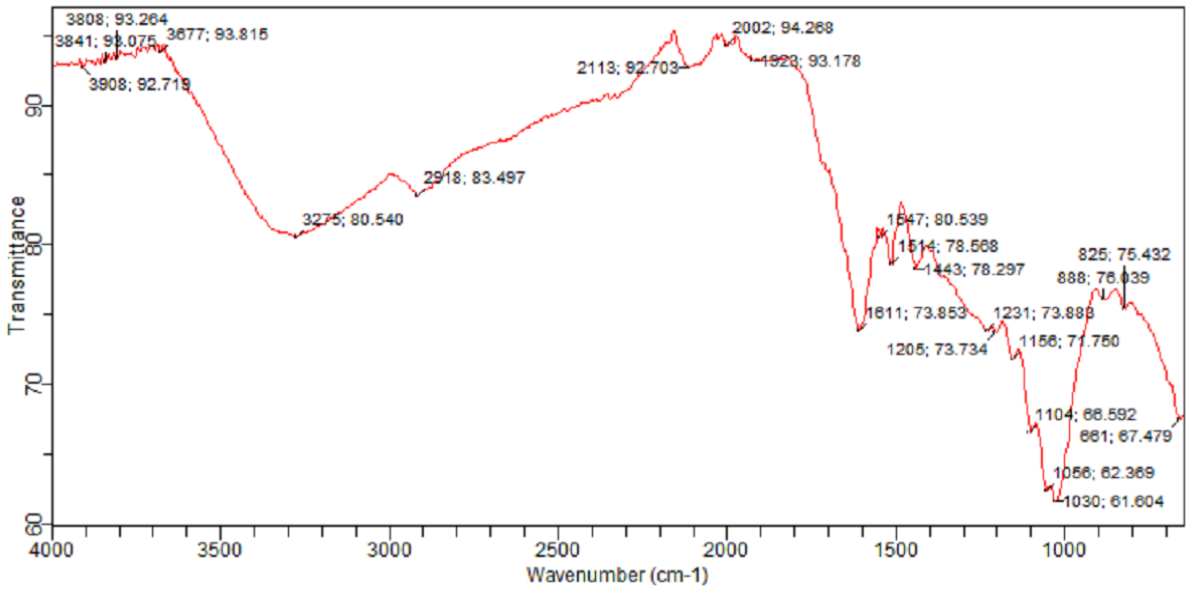

Figure 2. FTIR spectrum of MKP before adsorption

Table 2. FTIR Spectral Data and Assignment of MKP Before and After Adsorption by CR and MB

Before Adsorption MKP	After adsorption MKP-MB Loaded	Assignment
3275	3309(+34)	O-H stretching vibration in carboxylic acid groups (2500-3500cm^{-1})
2918	2921(+3)	O-H stretching vibration in carboxylic acid groups (2500-3500cm^{-1})
1611	1611(+0)	Benzene ring stretching in aromatic compounds (1615-1590cm^{-1})
1547	-	NO_2 in aliphatic nitro compounds due to antisymmetric stretching (1575-1545cm^{-1})
1030	1037(+7)	C-N stretching vibration in amines (1030-1330cm^{-1})
661	668 (+8)	O-C=O in carboxylic acid groups due to O-C=O bending (700-590cm^{-1}); C-C-CHO in aldehyde compounds due to C-C-CHO bending (695-635cm^{-1})

3.1.2. Scanning electron microscopy (SEM)

Scanning Electron Microscopy studies provide useful information regarding the surface morphology of the adsorbents. Generally the adsorbent with porous and rough morphology has high adsorption capacity [25]. The SEM images of the MKP before and after adsorption are presented in Figure 4 and 5, It can be seen that the pure MKP is more porous in nature rough surface with grain boundaries.. While the images of the adsorbent after adsorption shows reduction in the amount of pores present before adsorption, which is an evidence that adsorption have truly taking place.

Figure 4. SEM micrograph of MKP Before Adsorption

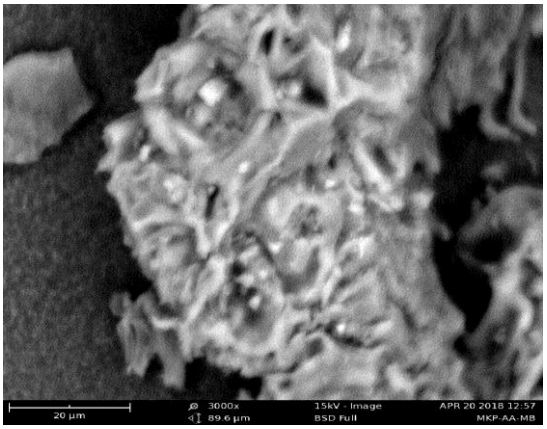

Figure 5: SEM micrograph of MKP after Adsorption of MB

3.2. Effect of Some Adsorption Parameters of The Dye on to the Adsorbent

3.2.1. Effect of contact time

In general, the rate of dye removal increases with an increase in contact time to a certain extent [26]. The range of observed contact time was 10min to 180min, the results revealed that the rate of dye removal gradually increases with an increase in time until it attained equilibrium. Due to deposition of dyes on the available adsorption site on adsorbent, any additional increase in contact time will not increase the uptake [27]. At this level, the amount of dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of dye being adsorbed by the adsorbent material. The time required to attain this state of equilibrium is referred to the equilibrium time (t_e) and the amount of dye adsorbed at the equilibrium time reflects the maximum percentage removal of the adsorbate under those operating conditions [28]. El-Sayed. [29] mentioned that contact time between adsorbent and adsorbate significantly affect the dye removal. Fig 6 shows the removal rapidly increases at the first 10 min and then slowly to obtain the equilibrium between MB on to MKP. The equilibrium obtained was at 150min for MB onto MKP. Similar result was obtained by Ihsan 2013, [30] in his work on the adsorption of methylene blue on to spent tea leaves where he obtained a contact time of 150 min.

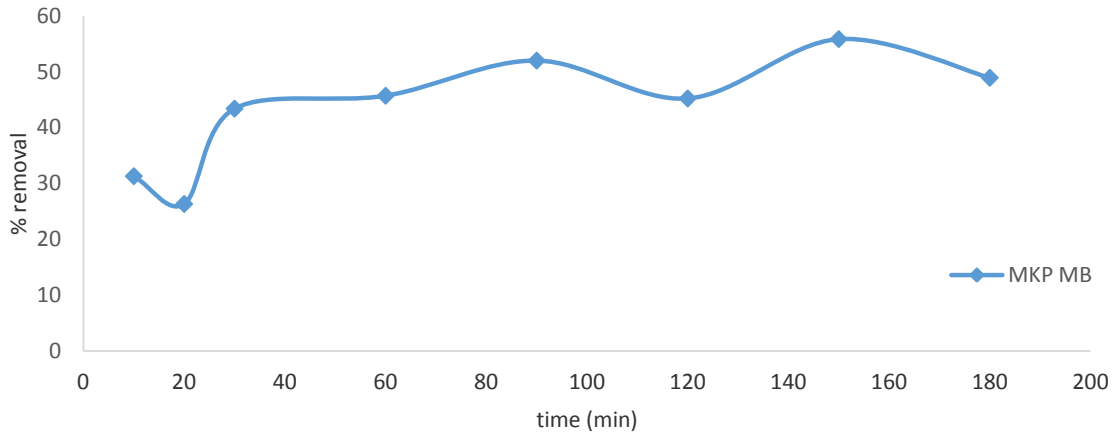

Figure 6. Effect of contact time on the adsorption of MB on to the MKP

3.2.2 Effect of Initial Dye Concentration

The effect of initial adsorbate concentration on the adsorption process was investigated by varying the initial adsorbate concentration between (5, 10, 20 0, 50, 70, 100, 120, 150) mg/l with constant adsorbent dosage of 0.2g and agitation rate of 200ms-1. The effect of initial dye concentration was plotted in Figure 7. As seen from Figure 7, the percentage dye removal increases with increasing the initial dye concentration from 5 to 10. It is because the active sites on the adsorbent surface are not fully occupied by the dye [31] and the adsorbent will adsorb the dye until it reaches its maximum adsorption capacity. However, the percentage of dye removal decreases after 10 mg/L of initial dye concentration. This is due to the adsorption capacity limitation of the adsorbent [32]. In other words, a given mass of adsorbent can only adsorb a certain amount of dye [33]. The higher the initial dye concentration, the lesser the percentage of dye removal [34]. It can be concluded that the percentage dye removal is highly dependent on the initial dye concentration.

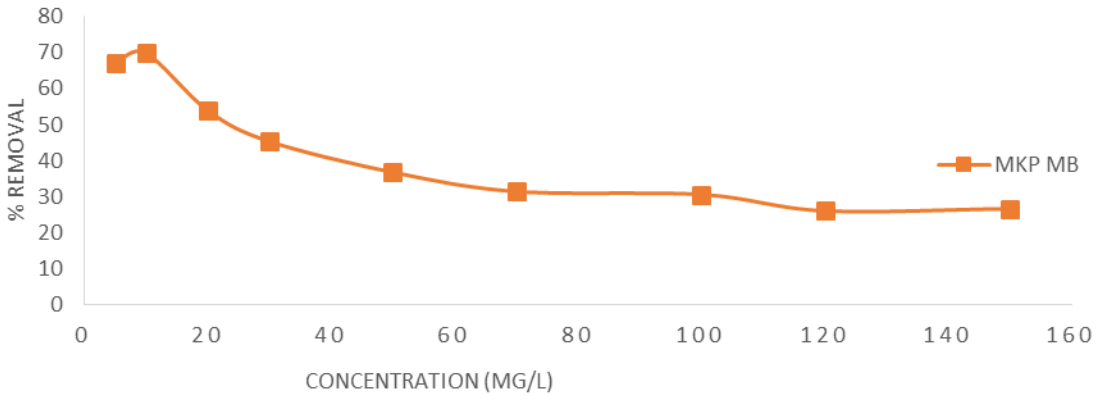

Figure 7: Effect of initial concentration of MB on to MKP.

3.2.3 Effect of Adsorbent Dosage

From Figure (8). It shows that the percentage of dye removal increases with increasing adsorbent dosage from 0.2 g to 0.7g. This is due to the greater availability of exchangeable sites or surface area at higher concentrations of the adsorbent [35]. It can be seen that the optimum percentage removal of MB on to MKP was 88.57% at. However, the

percentage dye removal decreases with the increase in adsorbent dosage after the optimum. This result is due to the overlapping of adsorption sites as a result of the overcrowding of adsorbent particles [36

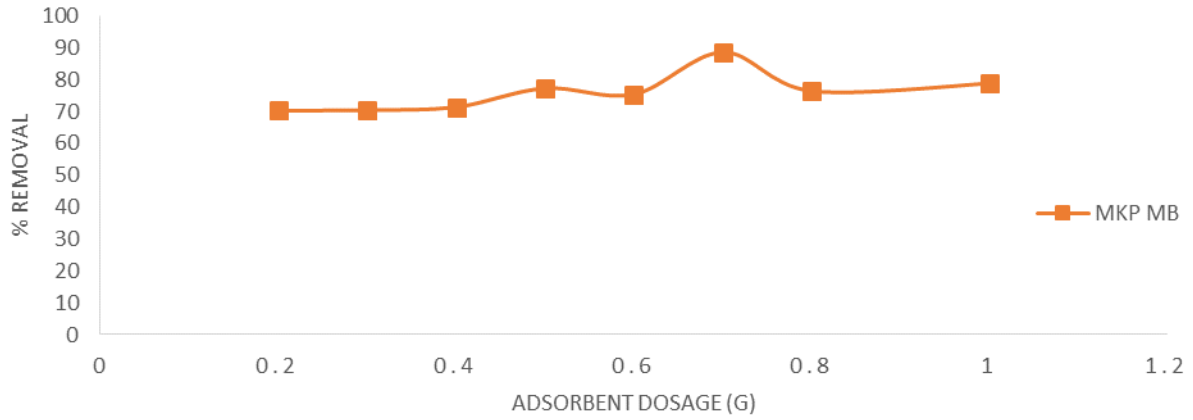

Figure 8: Effect of Adsorbent Dosage on the Adsorption of Dye on to the Adsorbent**.**

3.2.4. Effect of temperature

The plots in figure 9 show an increase in percentage removal with increase in temperature. Attesting to the fact that the lowest % removal was at the lowest temperature. These results affirm the endothermic nature of the adsorption process. [37].

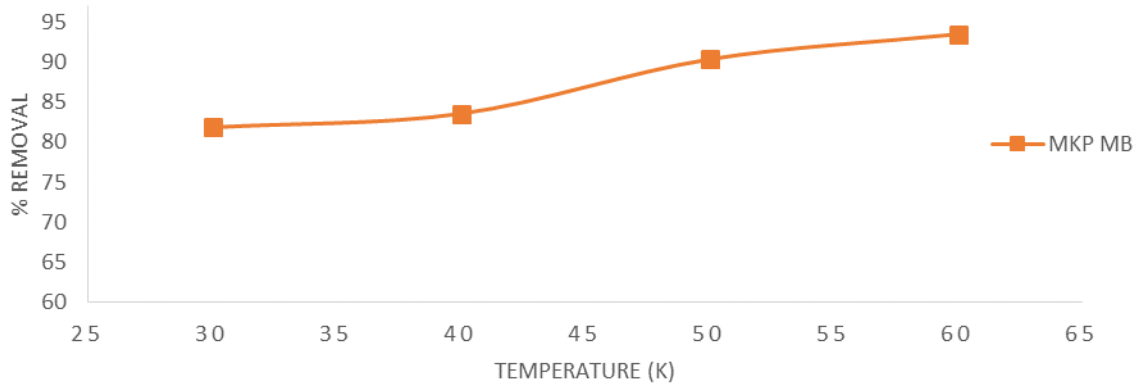

Figure 9: Effect of Temperature on the Adsorption of Dye on to the Adsorbent

3.3 Adsorption kinetics

To model the adsorption kinetics of MB onto MKP, 3 simple kinetic models were tested. The adsorption data was analyzed in terms of pseudo-first-order (PFO), pseudo second-order (PSO) mechanisms and Elovich model using equation 3, 4 and 5 respectively. The slope of the three graphs either pseudo first-order mechanism pseudo second-order mechanism or Elovich model that gave a linear relationship or having the highest correlation coefficient indicates which kinetics are applicable to the adsorption of MB on to MKP.

$\ln (q_e - q_t) = \ln q_e - k_1 t$ (3)

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

$$q = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (5)$$

Table 3: Kinetic Parameters for the removal of MB from Aqueous Solution onto the MKP.

Model	Kinetic parameter	Adsorbent
		MKP
	$q_{e,exp.}$(mg/g)	1.427
PFO	$q_{e,cal.}$(mg/g)	0.450
	k_1(min^{-1})	0.0033
	R^2	0.0728
PSO	$q_{e,cal.}$(mg/g)	1.384
	k_2(g/mg.min)	0.065
	R^2	0.9771
Elovich	α(mg/g.min)	0.722
	β(mg/g)	4.726
	R^2	0.7371

The adsorption parameters derived from the application of the pseudo-first-order equation (K1 and qe), the pseudo-second-order equation (K2, qe) and Elovich's equation (α and β) were calculated and are listed in Table 3. The plots of the adsorption kinetics are presented in Figure 6. The low correlation coefficients, R2, of the pseudo-first-order and Elovich models for both methods suggest that both models do not fit the experimental data. In addition, there is no agreement between the qe, experimental and qe calculated values for the pseudo-first-order model (Table 3). The correlation coefficients of the pseudo second-order model for the adsorption was 0.9771, which indicates the suitability of the pseudo second-order equation for the adsorption.

3.4. Adsorption isotherm

An adsorption/biosorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbents' surface at a given condition [16]. Adsorption isotherms are the mathematical equations in which the ratio between the adsorbate concentrations in the solid phase and that in the liquid phase at a constant temperature and pH is studied. In fact, it indicates how a substance from aqueous media transfers to a solid phase when an equilibrium state is established in a system [38]. In this study we consider 5 isotherms. The Langmuir, Freundlich, Dubinin and Radushkevich (D-R), Tempkin and Halsey.

3.4.3. D-R isotherm

From equation 9 a plot of lnq_eversus ⟦£ ⟧^2 indicates a straight line of slope ⟦B ⟧^and an intercept of lnq_s. The value was obtained using equation 10, the mean energy E of adsorption per molecule of adsorbate was calculated using equation 11.

3.4.1. Freundlich isotherm

Using equation 6, a plot of logqe vs. logCe results in a straight line with a slope of (1/n) and an intercept(k). Experimental data are often plotted in this manner as a convenient way of determining whether removal of material from solution is accomplished by adsorption and as means of evaluating the constants (k) and (n).

$$log_{q_e} = logk_f + \frac{1}{n} logC_e \qquad (6)$$

3.4.2. Langmuir isotherm

From equation 7 a plot of C_e/q_e versus C_e indicates a straight line of slope $1/q_{max}$ and an intercept of $1/K\ q_{max}$.

The fundamental characteristics of the Langmuir isotherm have been described by the term separation factor or equilibrium constant R_L, which is defined on different systems using equation 8

$$\frac{C_e}{q_e} = \frac{1}{kq_{max}} + \frac{C_e}{q_{max}} \quad (7)$$

$$R_L = \frac{1}{1+KC_0} \quad (8)$$

Where Co is the highest initial concentration of adsorbate, and K is its Langmuir constant. This indicates the nature of adsorption as reported by Hameed [39].

RL > 1(unfavorable) 0< RL < 1(favorable), RL = 0(irreversible), RL = 1(linear).

$$lnq_e = lnq_s - B\pounds^2 \quad (9)$$

Where q_e is D-R constant and $\pounds$ can be correlated as;

$$\pounds = RTln\left(1+\frac{1}{C_e}\right) \quad (10)$$

Where q_s is the maximum amount of adsorbate that can be adsorbed on adsorbent, B is the constant related to energy, and C_e is the equilibrium concentration (mg/L). R is universal gas constant, 8.314 $Jmol^{-1}K^{-1}$, T is the temperature (K). The mean free energy E of adsorption per molecule of adsorbate can be calculated using the following equation 11 [40]:

$$E = \frac{1}{\sqrt{2B}} \quad (11)$$

3.4.4. Temkin isotherm

From equation 12, a plot of q_e versus *In* C_e resulted in to obtaining the value of B and K_T which is the equilibrium binding constant (L/mg) corresponding to maximum binding energy from the slope and intercept respectively.

$$q_e = B_1 lnK_T + B_1 lnC_e \quad (12)$$

The constant K_T and B_1 in equation 12 can be calculated using a linear plot of q_e versus *In* C_e. K_T is the equilibrium binding constant (L/mg) corresponding to maximum binding energy.

3.4.5. Hasley:

From equation 13, a plot of $\ln q_e$ versus $ln\frac{1}{C_e}$ resulted in to evaluating the value of the constants n from the slope and K_H from the intercept respectively.

$$\ln q_e = \frac{1}{n} lnK_H - \frac{1}{n} ln\frac{1}{C_e} \quad (13)$$

Were K_H and n are Hasley isotherm constant and exponent, respectively. This equation is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of the adsorbent. lnq_e is plotted against $ln\frac{1}{C_e}$. [41].

Below are the plots of the adsorption isotherms figure 10, 11, 12, 13, 14.

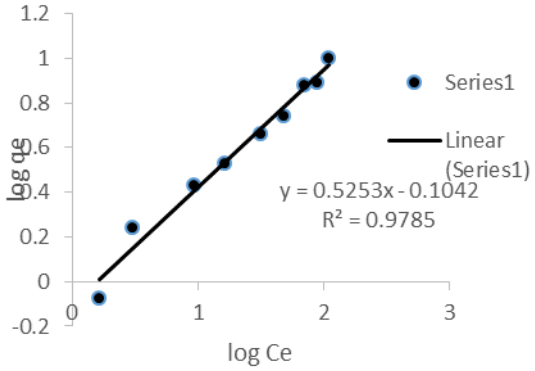

Figure 10: Langmiur adsorption isotherm for MB on MKP

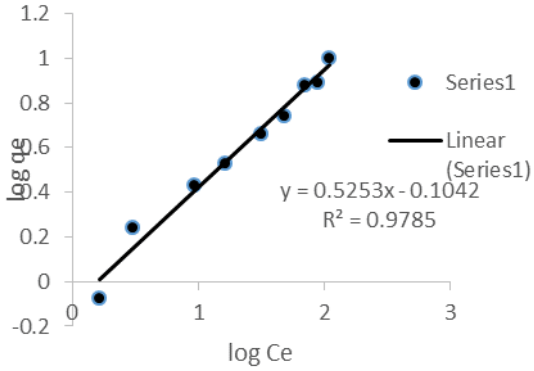

Figure 11: Freundlich adsorption isotherm for MB on MKP

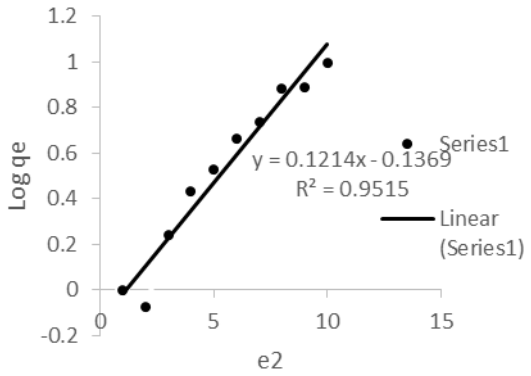

Figure 12. D-R adsorption isotherm for MB on to MKP

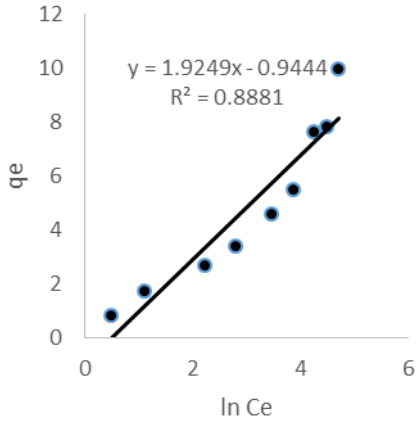

Figure 13. Temkin adsorption isotherm for MB on to MKP

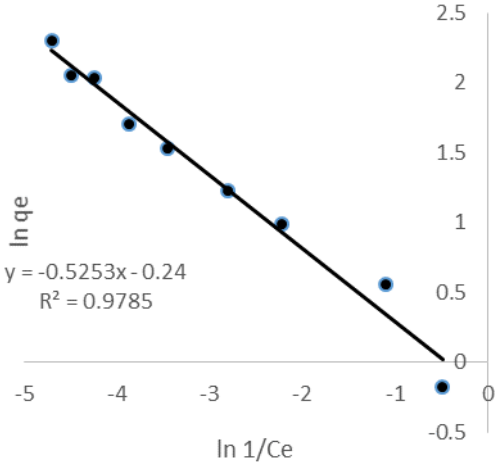

Figure 14: Hasley adsorption isotherm for MB on MK

MKP (t = 150min, C_o = 10mg/L, m = 0.2 g, T = 304.5 K). AKP (t = 90min, C_o = 10mg/L, m = 0.2 g, T = 304.5 K)

From table 4, it is clear that Freundlich isotherms best fits the adsorption process than the Langmuir isotherm, it is clear that the R^2 of the adsorption is close to unity which clearly indicates the experimented data follows it, suggesting multilayer coverage of the dye molecules at the surface of the adsorbent, [42]. The value of 1/n is a measure of surface heterogeneity or adsorption intensity and surface becomes more heterogeneous when its value gets closer to zero [43]. 1/n: is the adsorption intensity or surface heterogeneity. In general, as the K_F value increases the adsorption capacity

of adsorbent for a given adsorbate increases. The magnitude of the exponent, 1/n, gives an indication of the favorability of adsorption, the slope 1/n ranges between (0 and 1), becoming more heterogeneous as its value gets closer to zero. Values of n >1 represent favorable adsorption condition. [44].

Table 4: Isotherms Parameter for Adsorption of MB onto MKP and AKP

		Adsorbent
Isotherm	Parameters	MKP
Langmuir	R^2	0.9066
	q_0 (mg g^{-1})	11.136
	K_L (L mg^{-1})	0.030
	R_L	0.912
Freundlich	R^2	0.9785
	1/n	0.5253
	K_F (mg g^{-1})	0.7871
Temkin	R^2	0.8881
	B_T (mg L^{-1})	1.9249
	b (kJ mol^{-1}/ (mg L^{-1}))	1.316
	K_T (L mg^{-1})	0.999
Dubinin and	R^2	0.7278
Radushkevich	B (mol^2 kJ^{-2})	6^X10^{-7}
	Q_m (mg g^{-1})	2.074
	E (kJ mol^{-1})	9.560
Hasley	R2	0.9785
	n_H	1.904
	K_H	1.579

Hence, the value of 1/n of the adsorption indicate MB on to MKP's surface is heterogeneous. While n is greater than 1 which indicates favorability of adsorption, K_F value is roughly an indicator of the adsorption capacity of the adsorbent which can be defined as the adsorption or distribution coefficient, from the result obtained the K_F value of MB on to MKP is 0.7871mgg^{-1}. The adsorption process agrees with the Hasley adsorption model. Where k_H and n are the Halsey isotherm constant and exponent, respectively. The isotherm is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of the adsorbent, which the adsorption processes attest to [41].

3.5 Thermodynamic studies

Thermodynamic parameters are essential for the interpretation of the nature and characteristics of adsorption process concerning their physicochemical attributes. Gibbs free energy, adsorption enthalpy and entropy hold fundamental knowledge about the nature of adsorption. Gibbs free energy change (ΔG), provides the information of whether the adsorption process is spontaneous or not, meaning if it is necessary to give an external energy to the system in order to start the adsorption. Adsorption free enthalpy change (ΔH) gives the knowledge of the thermal character of the process, providing whether the process is endothermic or exothermic, and finally adsorption free entropy change

(ΔS) is an indicator of magnitude concerning the disorder among the adsorbate molecules and adsorbent. If ΔG < 0 (negative): it indicates that the adsorption process occurs spontaneously without the need for an external energy. If ΔG > 0 (positive), it means the adsorption does not take place spontaneously and the reaction mechanism needs a supportive force, mostly the heat energy. Usually, it is favorable for ΔG to be spontaneous (negative value) for ideal adsorption mechanism. The equilibrium constant Ke was calculated from the amount of MB adsorbed at equilibrium (Ci - Cf) and equilibrium concentration (Cf) of the MB in the liquid phase using equation 14

$$K_e = \frac{Q_e}{C_e} \quad (14)$$

Van't Hoff's equation 16 was employed to compute the values of ΔH and ΔS were obtained from the slope and intercept of the plot of lnk against 1/T as can be seen in figure 15 while values of ΔG at different temperatures were obtained using Eq. 15. [45].

$$\Delta G = \Delta H - T\Delta S \quad (15)$$

$$InK_l = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (16)$$

The Van't Hoof's plot of the adsorption process can be seen in figure 13 below

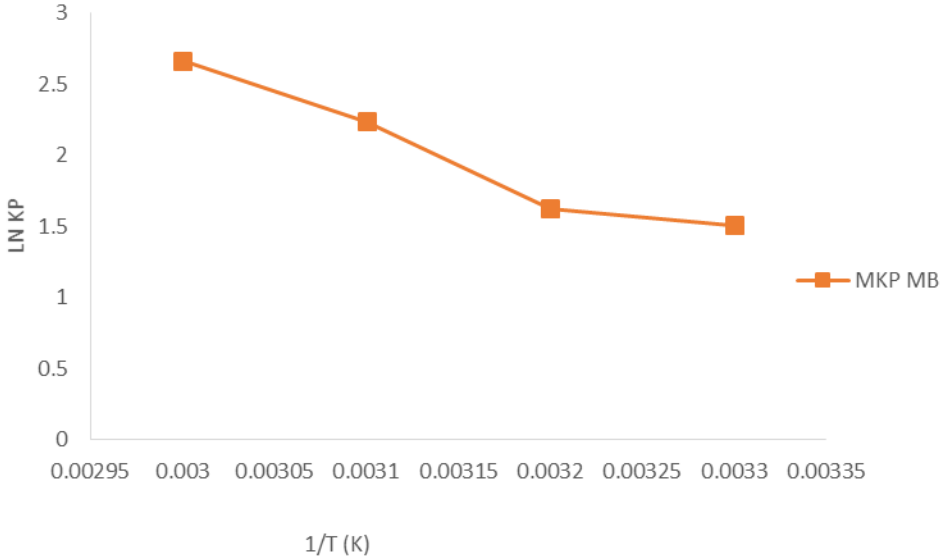

Figure 15: van't Hoff's Plot for Adsorption

The plot of lnK versus 1/T for van't Hoff's plot, gives the slope of ΔH/RT and the intercept of ΔS/R was used for the calculation of the above parameters from equation 14, 15 and 16 respectively.

Table 5. Thermodynamic Parameters for the Adsorption of MB on to MKP

Adsorbent-Adsorbate	ΔH (kJ/mol)	ΔS (kJ/molK)	ΔG (kJ/mo)			
			303	313	323	333
MB-MKP	33.252	0.121	-3.411	-4.621	-5.831	-7.041

MKP (t = 150min, C_o = 10mg/L, m = 0.7g).

The results obtained for the thermodynamic parameters are presented in Table 5 above. From the data provided in table 5 it will be seen that the adsorption process gives a negative ΔG that means the adsorption occurs spontaneously

without the need of an external energy. Analyzing the data presented in table 5, it can be seen that ΔH is all positive which confirms our previous endothermic assertion earlier under effect of temperature, meaning as the temperature increases the percentage removal increases. The degree of ΔH value provides the knowledge of adsorption characteristics, if ΔH value is between 8-25 kJ/mol, the adsorption process is a physisorption and if it is between 83 - 830 kJ/mol, it is a chemisorption from the data it is clear that adsorption of MB on to MKP is chemisorbed [46]. The negative values of ΔS for adsorbents, suggest decrease in randomness (freedom) of the molecules of the adsorbate on the solid surface of the adsorbents than in the solution, while the positive values of ΔS for the adsorbtion indicated an increase in randomness of the adsorbates molecules on the solid surface of the adsorbent than in the aqueous solution, and from the data in the table 4.4, it gives a positive value of ΔS.

4. Conclusion

Kolanut pod was chemically modified and tested for its efficiency in the adsorption of MB using batch process. The surface chemistry of the adsorbent was studied using FTIR and SEM were adsorption was concluded to have taken place. The parameters optimized on the course of the study are effects of contact time, initial concentration, adsorbent dosage and temperature, the results obtained virtually shows the significant effect on the process. The result shows that pseudo second-order kinetic model best fit the process, while the values of the thermodynamics parameters obtained indicate that the process is endothermic, spontaneous and Chemisorption. Adsorption of MB on to kolanut pod was found to best fit Freundlich and Hasley isotherm. These allow the conclusion that the chemically modified kolanut pod is an essential agricultural by product for the removal of MB.

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