

EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES ON BASIC DYE ADSORPTION USING COMPOSITE ACTIVATED CARBON

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Abstract— Batch adsorption experiments were carried out for the adsorption of cationic dye from aqueous solution onto composite activated carbon. The composite activated carbon was prepared from brewer's spent grain and sea bean shell at a ratio of 1:1. The equilibrium studies were done at different concentrations and temperatures. The equilibrium data were fitted to Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherm models. The results showed that both Langmuir and Freundlich isotherm model fitted the data reasonably well but Freundlich isotherm fitted better in the temperature range studied. This confirmed that the adsorption is heterogeneous, non-specific and non-uniform in nature. Kinetic studies were also undertaken in terms of first order, second order, pseudo first order, pseudo second order, Elovich, Boyd, and intra-particle diffusion models. The results indicated that the data followed pseudo second order model with surface adsorption and intra-particle diffusion concurrently operating during the adsorbate-adsorbent interaction. The values of the thermodynamic parameters computed from Van't Hoff plot confirmed the process to be endothermic and spontaneous in nature.

Key words— Activated carbon, basic dye, brewer's spent grain, sea bean shell.

I. INTRODUCTION

Several Industries generate wastewaters such as textile, chemical, refineries, plastics, and food processing plants. These wastewaters include residual dyes which are not biodegradable. It is estimated that more than 100,000 commercially available dyes with over 7×10^5 tonnes of dye stuff produced annually [1], [2], [3]. These residual dyes, when discharged into the environment, will become a serious threat. Generally, many dyes can be used in textile industry, like basic dyes, acid dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes, and sulphur dyes [4], [5]. Methylene blue (MB) is a basic dye heavily used in the textile industry [5].

Some specific effluents from industrial production processes may be difficult to purify by traditional wastewater treatment technology, as a result of the complexity of some of their components [6]. Many methods are used to remove dyes from wastewaters such as coagulation, membrane separation process, electrochemical, chemical oxidation, reverse osmosis, aerobic and anaerobic microbial degradation. These methods have restrictions, and therefore, are not successful for removing the color completely from wastewater [5], [7]. Among all these methods, adsorption is preferred due to its low cost and high treatment efficiency [8]

Activated carbon is the main adsorbent used in adsorption processes. The adsorption capacity of the activated carbon and also the performance of the activated carbon adsorption system are usually predicted from equilibrium sorption isotherm [9].

An adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid phase at a constant temperature and pH [10], [11], [12]. Experimental data were fitted into different isotherm models like; Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models.

The study of sorption kinetics in wastewater treatment is significant as it provides valuable insights into the reaction pathways and mechanisms of sorption reaction. Kinetics describe the solute uptake rate that controls the residence time of the sorbate uptake at the solid-solution interface, and are important because to design appropriate sorption treatment plants, the rate at which any pollutant is removed from aqueous solution must be predicted [13]. In this work, experimental data were fitted to first order, second order, pseudo first order, pseudo second order, Elovich Boyd and intra-particle diffusion models.

II. MATERIALS AND METHODS

A. Preparation of Activated Carbon

The spent grain used as one of the precursors was brought from Nigeria breweries Ninth Mile Enugu. It was collected immediately after use as a fresh spent grain. It was dried for 7 days under the sunlight to reduce the moisture content of the grain and after which it was packed until use. The hamburger seed shell was collected as a waste from Abakpa market, Enugu, Enugu state Nigeria.

B. Adsorbate

Methylene Blue (MB) (C1. 52015) with empirical formula $C_{16}H_{18}N_3SCl$ and formula weight of 319.9g/mol was supplied by De Cliff Integrated Ltd Ogbete Enugu, Enugu State Nigeria (97% purity). It has maximum absorbance at wavelength 661nm.

C. Preparation of Activated Carbon

The dried hamburger seed shell and spent grain were crushed to desired mesh size (1–2 mm) and then carbonized at 800°C for 2 hrs in a stainless steel vertical tabular reactor placed in a tube furnace. The char produced was crushed and sieved with 600µm sieve size. The char were soaked in 9M KOH solution with (1.1.5) char to KOH ratio. The mixture was then dehydrated in an oven at 105°C to remove moisture and then was activated under the same condition as carbonization, but to a different final temperature of 850°C for 1 hr. The activated products were then cooled to room

temperature and washed with hot deionized water and 0.1NHCl until pH of the washing solutions reached 6-7.

D. Adsorption Kinetic Model

The kinetic experiments were performed using a procedure similar to the equilibrium studies. 50mls of known concentration of MB was mixed with 0.02g of the adsorbent in a flask. Then, the flask was agitated in a shaker incubator for a contact time varied in the range 0- 240mins at a speed of 200rpm under room temperature. The adsorbent was separated from the solution by centrifugation and the filtrate was analyzed by the same procedure as batch equilibrium studies. The amount of MB adsorbed at each time interval per unit mass of the adsorbent, qt (mg/g), was calculated by equation 1:

$$qt = \left(\frac{C_0 - C_t}{W} \right) V \tag{1}$$

Where Co (mg/L) is initial MB solution, Ct (mg/L) is its concentration at time t, V (L) is the volume of the solution and W (g) is the mass of the adsorbent.

The kinetics of methylene blue adsorption was analysed using pseudo-first order model, pseudo-second order model, and intra particle diffusion model.

E. Adsorption Isotherm

Batch isotherm studies were carried out in 250ml conical flask at different temperature of 303K, 313K, 323K, 343K on an Isothermal shaker for 6 hours to ensure equilibrium. 0.02g of the adsorbent was mixed with 50ml of 30mg/l, 50mg/l, 80mg/l and 110mg/l of the solution at different pH of 4, 8 and 10. The pH was adjusted using 0.1M HCl or 0.1M NaOH before addition of the adsorbent. At the end of equilibrium time of 6 hours, the reaction mixture was centrifuged and the residual MB concentration analysed. The amount of MB adsorbent at equilibrium qe(mg/g) was calculated from the following equation (2).

$$q_e = \left(\frac{C_0 - C_e}{W} \right) V \tag{2}$$

F. Adsorption Kinetic Model

The adsorption kinetic produces valuable information about the reaction pathways and mechanism of the reactions. The kinetic of methylene blue adsorption was analysed using first order model, pseudo-first order model, second order model, pseudo-second order model, intra particle diffusion model, Elovich model and Boyd model.

1) First order Model

The adsorption kinetics can be described by a simple first order equation below:

$$CA_t = CA_0 e^{-k_1 t} \tag{3}$$

Linearization gives

$$\text{Log } CA_t = \frac{k_1}{2.303} (t) + \text{Log } CA_0 \tag{4}$$

Where Cat (mg/l) is the concentration of MB at time t, Cao (mg/l) is the initial concentration of MB. Ki is the rate constant of first order adsorption (h – 1) and t is the time gives in minutes. A plot of log Cat versus t gives slope of $\frac{k_1}{2.303}$ and intercept of LogCao.

2) Pseudo First Order Model

The pseudo first order equation is generally expressed as:

$$\frac{dq_t}{dt} = Kp_1 (q_e - q_t) \tag{5}$$

Integrating and rearranging gives:

$$\text{Log } (q_e - q_t) = \text{log } q_e - \frac{k_{p1}(t)}{2.303} \tag{6}$$

Where qe and qt are the amount of MB adsorbed (mg/g) at equilibrium and at time t, respectively and Kpi is the rate constant of pseudo-first order adsorption (min-1). A straight lines will be obtained by plotting $\text{Log}(q_e - q_t)$ against t. the values of the rate constant KI and qe were obtained from the slopes and intercepts of the plot

3) Second order Model

The typical second order model equation is given as:

$$\frac{dCA_t}{dt} = K_2 C^2 A_t \tag{7}$$

For the boundary condition of $t = dt$ to $t = t$ and $qt = 0$ to $qt = qt =$ Integrating and rearranging gives

$$1/CA_t = K_2 (t) + \frac{1}{CA_0}$$

Where CAO and Cat are the initial concentration of MB (Mg/l) and concentration at time t1 respectively. K2 is the rate constant of the second order (min-1). A plot of $1/CA_0$ Vs t gives K2 and $1/CA_0$ as slope and intercept respectively.

4) Pseudo Second order Equation

The pseudo second order adsorption kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \tag{8}$$

Integrating for the boundary conditions

$$t = 0 \text{ to } t = -t \text{ and } qt = 0 \text{ to } qt = qt$$

$$1/qt - qt = 1/q_e + Kp_2 t$$

Which can be rearranged as follows:

$$\frac{t}{qt} = \frac{1}{Kp_2 q_e^2} + \frac{1}{q_e} (t) \tag{9} \text{ and } h = Kq_e^2 \tag{10}$$

Where Kp2 is the rate constant of the pseudo second equation (1/min) qe and qt are the sorption capacity at equilibrium and time t (mg/l). h is the initial sorption rate. A plot of t/qt versus (t) gives 1/qe and $1/Kp_2 q_e^2$ as slope and intercept.

5) Intra Particle Diffusion Model

Weber-Morris found out that in many adsorption cases, solute uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time, t. the model is expressed as:

$$qt = kidt^{1/2} + C$$

Where Kid is the intra particle diffusion rate constant (mg/gh^{1/2}). Plotting qt versus $t^{1/2}$ will give slope of kid and intercept C (mg/g). Value of C gives the idea about the thickness of boundary layer ie the larger the intercept, the greater the contribution of the surface sorption in the rate controlling step.

6) Elovich Model

The Elovich equation has been successfully applied to represent chemisorptions processes and at low adsorption rate. The equation is as follows:

$$\frac{dq_t}{dt} = x e^{-Bqt} \tag{11}$$

Integrating with suitable boundary conditions gives:

$$qt = \frac{1}{\beta} \ln(X\beta) + \frac{1}{\beta} \ln(t) \tag{12}$$

Where x is the initial sorption rate constant (mg/gml), and parameter β is related to the extent of the surface coverage and

to the activation energy of chemisorptions (g/mg). The constant can be obtained from the plot of qt versus Lnt as the slope and the intercept. The correlation coefficients were better but still lower than that of pseudo second order model.

7) Boyd Model

In order to determine the actual rate controlling step involved in sorption process, Boyd model is used which is as follows:

$$F = 1 - \frac{6}{n^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \exp[-m^2 \beta t] \quad (13)$$

Where F is the fractional attainment of equilibrium at time t, and is obtained by the expression: $F = qt/q_e$ where qt(mg/g) is the amount of sorbate taken up at time t, and q_e (mg/g) is the maximum equilibrium uptake and $\beta t = Di(\pi^2/r^2)$ (14)

βt is time constant (min⁻¹) of the sorbent particle (cm), assumed to be spherical and m is an integer that defined the finite solution hence, βt is given by the equation

$$\beta t = -0.4977 - \ln(1 - F) \quad (15)$$

Thus, the value of βt can be computed for each value of F1 and then plotted against time, t.

G. Adsorption isotherm Models

Adsorption isotherm equations are models describe experimental sorption data. It helps to understand the nature of the interaction between the adsorbate and adsorbent used for the adsorption. An adsorption isotherm describes the relationship between the amount of adsorbate uptaken by the adsorbent and the adsorbate concentration remained in the solution [14], [15]. The equation parameter and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into the adsorption mechanism, the surface properties of an adsorbent and affinity of the adsorbate for an adsorbate [16], [15], [17], [18]. In this study, the experimental results were fitted to langmuir, freudlich, Temken Dubinin – Radush Kevich Isotherms.

1) Langmuir Isotherm

The Langmuir adsorption isotherm describes quantitatively the build-up of a layer of molecules on an adsorbent surface as a function of the concentration of the adsorbed material in the liquid in which it is in contact [19]. This isotherm is based on the assumption that the adsorption process takes place at specific homogenous sites within the adsorbent surface and that once a dye molecule occupies a site, no further adsorption can take place at that site which concluded that the adsorption process is monolayer in nature [18]. The isotherm can be written as:

$$\frac{q_l}{q_0} = \frac{q_l C_{Ae}}{1 + K_L C_{Ae}}$$

The linear form of the isotherm is given as:

$$\frac{C_{Ae}}{q_e} = \frac{1}{q_0 K_L} + \frac{C_{Ae}}{q_0} \quad (16)$$

Where q_e is the amount of adsorbate adsorbed per gram of the adsorbent (mg/g), C_{Ae} is the concentration of adsorbate in liquid equilibrium, (mg/l). the constant K_L and q_0 relate to energy of adsorption and maximum adsorption capacity respectively. K_L is a measure of heat of adsorption utilized to calculate dimensionless separation parameter $K_L q_0$ is in mg/g.

To determine if the adsorption process is favourable or unfavourable, for the Langmuir type adsorption process, the

isotherm shape can be classified by a term “RL” a dimensionless constant separation factor which is defined as below [20].

$$R_L = \frac{1}{(1 + K_L C_{A0})} \quad (17)$$

Where K_L (L/mg) is the Langmuir constant and C_{A0} is the lowest initial solute concentration (mg/l). a plot of C_{A0} / q_e versus C_{Ae} from the linear relationship of the model will give $1/(q_0 K_L)$ and $1/q_0$ as intercept and slope respectively.

2) Freundlich Isotherm

The Freundlich Isotherm equation is based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption site [21]. This isotherm does not predict any saturation of the sorbent by the sorbate, indicating multilayer sorption of the surfaces [22]. The Freundlich isotherm is expressed by the following equation.

$$q_e = K_F C_{Ae} \quad (18)$$

A linear form of the freudlich can be obtained by taking the logarithm to the above equation.

$$\log q_e = \log K_F + \frac{1}{n} \log C_{Ae} \quad (19)$$

Where K_F = freundlich constant. Where K_F (mg/g) is the constant related to the adsorption capacity. The value of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogenous as its value gets closer to zero [23]. A plot of $\log q_e$ versus C_{Ae} will give intercept as $\log K_F$ and slope as $1/n$.

3) Temkin Isotherm Model

The heat of the adsorption and the adsorbate – adsorbate interactions in a adsorption process were studied by Temkin and Pyzhev [24], and its equation is given as follows:

$$q_e = B \ln A + B \ln C_e \quad (20)$$

$$B = (RT/b)$$

Where T is the absolute temperature in K and R is the universal gas constant 8.3143J/mol.k. The constant b is related to the heat of adsorption q_e (mg/g) and C_e (mg/l) and the equilibrium concentration respectively. A and B are constants related to adsorption capacity and intensity of adsorption. A plot of q_e versus $\ln C_e$ yields a slope of B and intercept of $B \ln A$.

4) Dubinin – Raduschkevich (D – R)

Dubinin – Radushkevich model is similar to the Langmuir model but does not assume a homogenous surface or constant energy potential [21]. The D – R equation can be written as:

$$q_e = \varepsilon_{max} \exp(-B_D \varepsilon^2) \quad (21)$$

Where ε is the Polanyi potential (J/mol) given by:

$$\varepsilon = RT \ln(1 + 1/C_e)$$

Linearizing it gives

$$\ln q_e = \ln q_{max} - 2B_D RT \ln(1 + 1/C_e)$$

Where q_e is the amount of sorbate adsorbed at equilibrium (mg/g), q_{max} is the theoretical saturation capacity (mg/g), B_D is a constant related to the adsorption capacity (mg²/l²). A plot of $\ln q_e$ versus $(RT \ln(1 + 1/C_e))$ yields a straight line with a slope of -2BD and intercept of $\ln q_{max}$. The value of BD can be used to calculate the sorption mean free energy E (KJ/Mol).

$$E = (2B_D)^{-1/2}$$

Taking the logarithm of the D – R equation, it becomes

$$\ln q_e = \ln q_{max} - 2B_D \varepsilon \quad (22)$$

A plot of $\ln q_e$ against ε gives slope of -2BD and intercept of $\ln q_{max}$.

III. RESULTS AND DISCUSSION

KINETIC EQUATION	pH	KINETIC PARAMETERS	R ²
First Order Kinetics	2	K ₁ = -0.0046 (min ⁻¹)	0.796
	4	K ₁ = -0.0046 (min ⁻¹)	0.739
	6	K ₁ = -0.0069 (min ⁻¹)	0.797
	8	K ₁ = -0.0069 (min ⁻¹)	0.887
	10	K ₁ = -0.0046 (min ⁻¹)	0.796
Second order Model	2	K ₂ = 0	0.852
	4	K ₂ = 0.003	0.852
	6	K ₂ = 0.017	0.871
	8	K ₂ = 0.039	0.904
	10	K ₂ = 0.020	0.876
Intra – Particle Diffusion Model	2	K _{id} = 1.9267 (min ⁻¹), C = 38.917	0.8365
	4	K _{id} = 0.5807 (min ⁻¹), C = 65.187	0.7186
	6	K _{id} = 0.3089 (min ⁻¹), C = 70.297	0.8198
	8	K _{id} = 0.0986 (min ⁻¹), C = 73.352	0.8959
	10	K _{id} = 0.0919 (min ⁻¹), C = 73.362	0.822
Elovch Model	2	β = 0.108g/mg, α = 16.145mg/g.min	0.941
	4	β = 0.351g/mg, α = 2.992mg/g.min	0.861
	6	β = 0.693g/mg, α = 1.474mg/g.min	0.887
	8	β = 2.288g/mg, α = 0.439mg/g.min	0.874
	10	β = 2.273g/mg, α = 0.442mg/g.min	0.936
KINETIC EQUATION	INTERCEPT		R ²
Boyd Model	2	-0.165	0.972
	4	1.372	0.961
	6	1.813	0.929
	8	2.837	0.873
	10	3.208	0.976

TABLE 1. KINETICS PARAMETERS

Pseudo First order					Pseudo – Second order			
pH	Quexp(mg/g)	Qualc(mg/g)	K ₁ (min ⁻²)	R ²	IKP2(min ⁻¹)	H	Qe(mg/g)	R ²
2	64.549	20.09	0.0161	0.767	KP ₂ = 0.001	5.102	71.429	0.998
4	72.687	3.313	0.0092	0.364	KP ₂ = 0.005	29.586	76.923	1.0
6	74.3575	1.5922	0.0046	0.132	KP ₃ = 0.009	53.28	76.923	1.0
8	74.7223	0.5688	0.0023	0.030	KP ₃ = 0.024	42.012	76.923	1.0
10	74.5688	0.3515	0	0.006	KP ₃ = 0.034	201.183	76.923	1.0

TABLE 2. KINETICS PARAMETERS

A. Kinetics models

The study of sorption kinetics in wastewater treatment is significant as it provides valuable insights into the reaction pathways and mechanisms of sorption reaction

1) First order kinetics

In order to determine the controlling mechanism of adsorption process such as transfer and chemical reaction, the first order kinetic model was used to test the experimental data. The values of rate constant were calculated from the slopes of the graphs plotted and they are presented in table (1). The low correlation coefficient (R²) obtained at different pH values showed poor agreement of the first order model with the experimental data.

2) Pseudo-first order

The pseudo-first order parameters at different pH along side with their correlation coefficients (R²) are shown in table (2). The R² values obtained were small at all the pH studied, and the experimental q_e values did not agree with the calculated values obtained from the linear plots (table 2).

3) Second order model

The values of the correlation coefficients, were relatively small compared to the pseudo second order meaning that the model did not fit the experimental values well.

4) Pseudo second order

The values of q_e and K were obtained from the slope and intercept. The values of the rate constants, correlation coefficients, the experimental and calculated values are shown in table 2.

It can be seen that the correlation coefficients for the linear plot of the pseudo second order increased from 0.988 to 1 as the pH increased, which is higher than the correlation coefficients of all other models studied. Also, there is a good agreement between the experimental q_e values and the calculated q_e values. This indicates that the adsorption kinetic is better represented by the pseudo-second order model. The high initial sorption rate, h, obtained showed that the adsorption was rapid. The uptake of adsorbate by adsorbent has been observed to occur in two stages: the first rapid and quantitatively predominant and the second slower and quantitatively insignificant [25], [26]. The rapid adsorption of MB by this adsorbent is probably due to the abundant availability of active sites on the biomass, and the perceived porous and mesh structure of the adsorbent which provides ready access and large surface area for the adsorption of MB dye on the binding sites [27], [28].

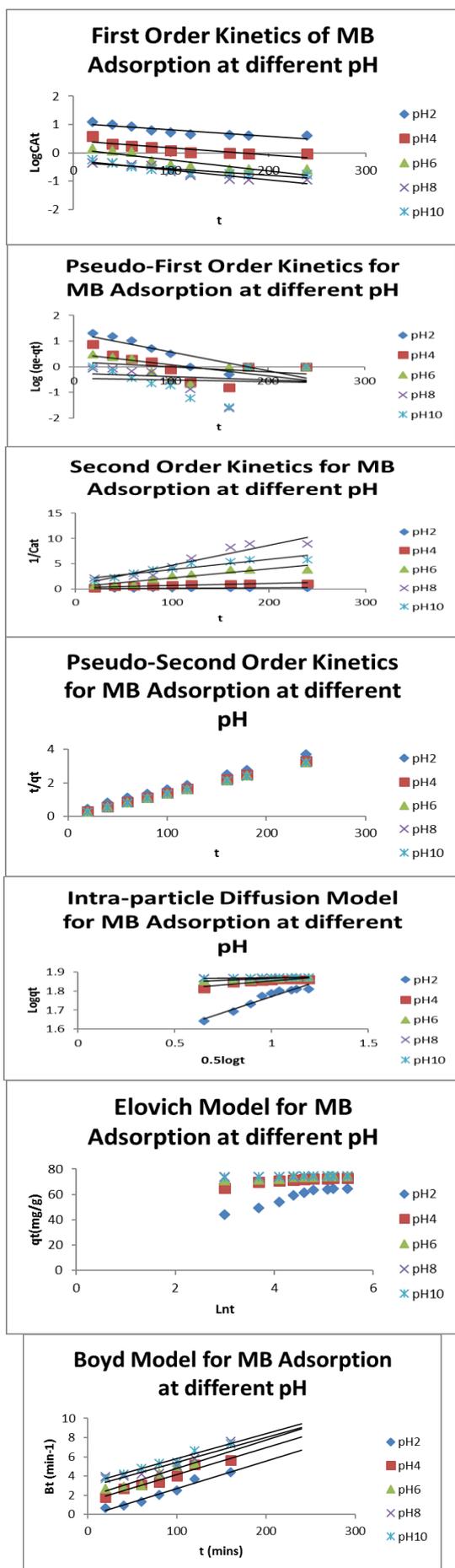


Fig. 1. Kinetics plots

5) Intra particle diffusion

The intra particle diffusion model was proposed to identify the adsorption mechanism and to predict the rate controlling step. The intra particle diffusion model usually includes three steps. The first portion is the external surface adsorption or boundary layer diffusion. The second portion is the gradual stage of adsorption which is the intra particle diffusion. If the plot of q_t versus $t^{1/2}$ is linear and passed through the origin, then the intraparticle diffusion is the rate-controlling step [29]. The third portion is the final equilibrium stage in which the intra particle diffusion starts to slow down due to the extremely low dye concentration left in the solution [28].

The plot shows that the linear plot did not pass through the origin which indicated that the intra particle diffusion was not only the rate controlling step and the boundary layer diffusion controlled the adsorption to some extent [48]. This deviation may be due to the difference in mass transfer rate in the initial and final stage of adsorption [29], [30].

The values of C and K_{id} are given in Table 1. The values of the intercept C increased with an increase in pH, which showed that boundary layer effect increased as pH increases.

The correlation coefficients for intraparticle diffusion were lower than that for the pseudo second order kinetics which showed that the present system may be followed by intraparticle diffusion, but is not the only rate controlling step.

6) Boyd model

A linear plot of Bt against t , passing through the origin implies that pore-diffusion controls the rate of mass transfer. However, if the plot is non linear or linear but does not pass through the origin film-diffusion or chemical reaction dominate the adsorption rate [31], [32], [33].

Boyd model was used to investigate the contribution of film resistance to the kinetics of MB sorption. The model assumes that the main resistance to diffusion is the boundary layer surrounding the adsorbent particle.

The latter seems to be the case in MB adsorption on the composite adsorbent as shown in figure. However, it seems the pore diffusion becomes more important at lower pH, as the intercept approaches 0 with decrease in pH as indicated on table (1). The correlation coefficient is equally reasonable, but still, they are lower than that of pseudo second order model.

B. Isotherm models

An adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid phase at a constant temperature and pH.

1) Langmuir

The value of the separation factor (RL) indicates the nature of adsorption process. RL values indicates the type to be irreversible ($RL = 0$), favourable ($0 < RL < 1$), linear ($RL = 1$) or unfavourable ($RL > 1$). The linear plot of ce/q_e vs ce indicated the applicability of Langmuir adsorption isotherm. Consequently, suggested the formation of mono layer coverage of the adsorbate on the surface of the adsorbent [34]. Langmuir constants, q_0 and K_L were calculated from the slopes and intercepts are given in table 3 along with the correlation coefficient (R^2) and separation factor (RL). From the table, it is clear that the K_L values were higher at higher temperature, which showed endothermic nature of MB adsorption. The average values of RL for each of the temperature and pH used

were between 0 and 1, which indicated the favourable adsorption of MB. This was in agreement with the work done by Dalia Khalid et al on the batch adsorption of basic dye using acid treated kenaf fiber [29], work done by Emad N. ElQada et al in adsorption of methylene blue into activated carbon form [35], I.A.W Tan et al on equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon [36] etc.

2) *Freundlich isotherm*

The values of Freundlich constants and correlation coefficients (R²) are given in table 3. The values of K_f and n changed with the rise in temperature. The value of n showed an indication of the favourability of adsorption. Values of n larger than 1, showed the favourable nature of the adsorbent [34], [37], [38]. The value of n suggested that MB was favourably adsorbed by the activated carbon prepared from Hamburger seed shells. The correlation coefficients greater than 0.980 showed that the data fitted well with Freundlich equation was statistically confirmed by giving greater R² values closer to unity (0.85 – 0.999). This implies that Freundlich model may better describes an adsorption isotherm for the adsorbent. This adsorptive behaviour indicates that the adsorption takes place on a heterogeneous surface, which may be attributed to the various active sites on the adsorbent [39]. This was in line with the work done by Hui Deng et al on adsorption of methylene blue in adsorbent materials produced from cotton stalk [40].

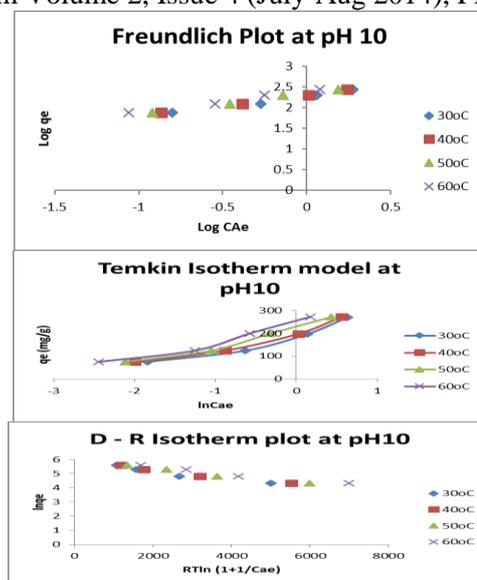
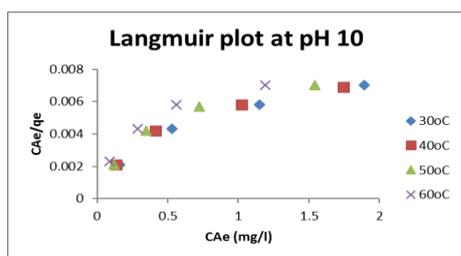


Fig. 2. Isotherm plots

3) *Temkin isotherm*

The linear isotherm constants and coefficients of determination are presented in table 4. It shows that the equilibrium binding constant (A) (l/mg) which corresponds to the maximum binding energy increased with increase in temperature and was maximum at pH of 10. The constant b which is related to the heat of adsorption, equally increased with increase in temperature. The results implied that the affinity of the binding sites for MB increased with increase in temperature. Examination of the data shows that the Temkin Isotherm is applicable to the MB adsorption onto hamburger activated carbon judged by high correlation coefficient (R² ranged from 0.915 to 0.985).

TEMPERATURE		LANGMUIR CONSTANT			FREUNDLICH CONSTANT			
TEMP(K)	q ₀ (mg/g)	K _L (L/mg)	R _L	R ²	1/n	n	K _F	R ²
303	pH ₄ 0	0	1.0	0.997	0.859	1.164	78.7	0.999
	pH ₁₀ 500	1.0	0.032	0.923	0.517	1.934	185.35	0.989
313	pH ₄ 1000	0.25	0.118	0.701	0.765	1.307	164.8	0.987
	pH ₁₀ 500	2.0	0.016	0.950	0.501	1.938	198.6	0.994
323	pH ₄ 500	1.0	0.032	0.933	0.652	1.534	193.2	0.997
	pH ₁₀ 500	2.0	0.016	0.980	0.516	1.980	221.8	0.990
333	pH ₄ 500	1.0	0.032	0.991	0.608	1.645	213.8	0.985
	pH ₁₀ 500	2.0	0.016	0.967	0.505	1.996	251.2	0.997

TABLE 3: ISOTHERM CONSTANTS FOR MB ADSORPTION ON COMPOSITE ADSORBENT

	TEMKIN CONSTANT				DUBININ-RADUSHKEVICH CONSTANT			
	B	A	b	R ²	Q _m (mg/g)	B _D	E(KJ/mol)	R ²
303	pH ₄ 126.5	1.8	19.9	0.976	421.6	5 x 10 ⁻⁴	3.1..6	0.986
	pH ₁₀ 76.23	13.6	33.0	0.924	333.6	15 x 10 ⁻⁴	5.7.7	0.951
313	pH ₄ 112.1	5.1	23.2	0.915	435.3	2.5 x 10 ⁻⁴	4.472	0.958
	pH ₁₀ 74.55	16.6	34.9	0.946	343.8	1.5 x 10 ⁻⁴	05.77	0.972
323	pH ₄ 97.16	8.3	27.6	0.954	411.6	2 x 10 ⁻⁴	5.0.0	0.979
	pH ₁₀ 77.85	18.4	34.9	0.967	376.2	1.5 x 10 ⁻⁴	5.777	0.984
333	pH ₄ 92.87	10.9	29.8	0.985	428.8	1.5 x 10 ⁻⁴	5.77	0.994
	pH ₁₀ 75.83	25.3	36.5	0.951	389.2	1 x 10 ⁻⁴	7.0.7	0.926

TABLE 4: THERMODYNAMIC PARAMETER FOR MB ADSORPTION AT PH4

Concentrations (mg/l)	$\Delta G(\text{KJ/mol}) P^{\circ}$				$\Delta H(\text{KJ/mol})$	$\Delta S(\text{Jmol}^{-1}\text{K}^{-1})$
	30°C	40°C	50°C	60°C		
30mg/l	-11.556	-13.410	-15.264	-17.118	44.621	0.1854
50mg/l	-11.221	-12.844	-14.468	-16.092	37.978	0.1624
80mg/l	-11.009	-12.538	-14.067	-15.596	35.318	0.1529
110mg/l	-11.104	-12.283	-13.461	-14.640	24.618	0.1170

AT pH₁₀

Concentrations (mg/l)	$\Delta G(\text{KJ/mol})$				$\Delta H(\text{KJ/mol})$	$\Delta S(\text{Jmol}^{-1}\text{K}^{-1})$
	30°C	40°C	50°C	60°C		
30mg/l	-15.424	-16.464	-17.504	-18.544	16.088	0.104
50mg/l	-13.642	-14.652	-15.662	-16.672	16.961	0.101
80mg/l	-12.827	-13.947	-15.067	-16.187	21.109	0.112
110mg/l	-12.395	-13.225	-14.055	-14.885	12.754	0.083

4) Dubinin-radushkevich model

The Langmuir Isotherm constants do not give any information concerning the chemical or physical properties of the sorption. But the calculated sorption mean free energy E, from the D-R isotherm gives information about the chemical or physical properties of the sorption [19]. The values of the mean adsorption energy that is less than 8kj/mol, revealed that the adsorption of MB was predominantly a physical process rather than a chemical one [37], [41]. The correlation coefficient of the isotherm showed that D-R equation represents a good fit of the experimental data (Table 4).

Moreover, the maximum adsorption capacity q_m obtained using D-R isotherm for adsorption of MB is 435.3mg/g, which is close to half of that obtained (1000mg/g) from Langmuir isotherm model (Table 4).

C. Adsorption thermodynamics

The thermodynamic parameters of the adsorption process were determined from the Van't Hoff equation by plotting lnK_D versus 1/T for different temperature at 303,313, 323 and 333K as follows:

$$\Delta G^{\circ} = \Delta H - T\Delta S \quad (23)$$

$$\ln K_c = -\Delta H/RT + \Delta S/R \quad (24)$$

Where K_c is the equilibrium constant, which is the ratio of the equilibrium concentration of the dye ion on the adsorbent to the equilibrium concentration of the dye ions in solution. R is the universal gas constant (8.314J/kmol), T (k) is the absolute temperature. ΔH represents the difference in binding energies between the adsorbent and the adsorbate (solute) and between the solvent and the solute.

The values of ΔS° and ΔH° were obtained from intercept and slope respectively of plot of lnK_c against 1/T.

The negative values of ΔG° (table 5) indicated the feasibility of the process and the spontaneous nature of the adsorption. The value of ΔG° became more negative with increasing temperature. This showed that increase in temperature was favourable for the removal process. The results also showed that both enthalpy and entropy values were positive at different concentration, signifying that the adsorption process was endothermic and the degree of dispersion increased with increase in temperature. The endothermic behaviour observed from enthalpy value further confirmed the trend of adsorption of MB on the adsorbents which were found to increase as temperature was increased. The nature of the adsorption process was confirmed by the magnitude of the ΔH° values. It is accepted that if magnitude of

enthalpy change is less than 84Kj/mol, adsorption is physical, however, chemisorptions takes place from 84 to 420Kj/mol. The range of values of ΔH° from table 5 showed that the nature of adsorption is physical.

IV. CONCLUSION

The composite activated carbon used for this study was prepared from brewer's spent grain and sea bean shell at a ratio of 1:1. The result of this study can be summarized as follows;

- The developed composite activated carbon is a promising adsorbent for removal of cationic dye from solution.
- The experimental data showed perfect fit with the Freundlich isotherm, which confirm that the adsorption process is heterogeneous, non- specific and non-uniform in nature. Therefore, the mechanism of adsorbate-adsorbent interaction is complicated involving a wide range of sites differing in a number of aspects including energy considerations.
- The kinetic study was investigated using first order, pseudo first order, second order, pseudo second order, Elovich, Boyd and intra-particle diffusion models. The result indicates that adsorption kinetics followed the pseudo second order with the intra- particle diffusion model as one of the rate limiting step.
- The sorption process was found to be endothermic in nature with negative value of the entropy.
- The negative value of the Gibbs free energy and positive value of the enthalpy suggested the adsorption to occur by physical process.

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