



RESEARCH ARTICLE

EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES OF ADSORPTION OF METHYLENE BLUE ON ACTIVATED CARBON FROM COCOA POD SHELLS

Akissi Lydie Chantal Koffi, Djamatché Paul Valéry Akesse, Herman Yapi Yapo, David Léonce Kouadio, Kouakou Séraphin Konan and Bini Kouamé Dongui

Laboratory for Environmental Science and Technology, Jean Lorougnon GUEDE University, Daloa, Côte d'Ivoire.

Manuscript Info

Manuscript History

Received: 05 September 2021

Final Accepted: 10 October 2021

Published: November 2021

Key words:-

Adsorption, Methylene Blue, Kinetics, Isotherm, Thermodynamics

Abstract

The aim of this research is to investigate the feasibility of using activated carbon from cocoa pod shells, waste from agriculture to adsorb methylene blue from aqueous solutions through batch tests. Various physiochemical parameters such as, contact time, initial dye concentration, adsorbent dosage, pH of dye solution and temperature were investigated in a batch-adsorption technique. The process followed the pseudo-second order kinetics model which showed chemical adsorption. Langmuir and Freundlich isotherm models were used to determine adsorption constants. The maximum adsorption capacity at 30°C is 526.31 mg/g. Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) were studied, and the adsorption process of BM was found to be exothermic and spontaneous.

Copy Right, IJAR, 2021., All rights reserved.

Introduction:-

The main sources of water contamination are industrialization, agricultural activities and other environmental and global changes. Textile industries produce a lot of wastewater, which contains a number of contaminants, including acidic or caustic dissolved solids, toxic compounds, and any different dyes. Many of these dyes are carcinogenic, mutagenic, and teratogenic and also toxic to human beings, fish species, and microorganisms (Aljebore et al, 2017). Synthetic dyes are commonly used in many industries such as textile, leather, tanning, paper, rubber, plastics, cosmetics, pharmaceutical and food industries.

Several methods were applied to remove textile dyes prior to discharge into water such as adsorption (Sakr et al., 2015), photocatalysis (Jawad et al., 2015), oxidation (Nidheesh et al., 2018), and coagulation (Beluci et al., 2019). Adsorption is considered as the best wastewater treatment method due to its universal nature, inexpensiveness and ease of operation (Aminu and Sulaima, 2019). Adsorption can also remove soluble and insoluble organic pollutants. Activated carbon (AC) is known for its superior surface areas and microporous structures, which contribute to their higher adsorption capacities. Thus, its wider applications as adsorbent can be attributed to such properties (Bello et al., 2019).

Although adsorption technologies are well established, a significant limitation is the cost of adsorbent materials. This has motivated the search for low-cost and renewable materials for use as adsorbents and has led to a growing interest in the use of nonconventional and locally available materials such as natural materials and agricultural wastes. Therefore, many researches in recent years have focused on the use of various low-cost adsorbents instead of

Corresponding Author:- Akissi Lydie Chantal Koffi

Address:- Laboratory for Environmental Science and Technology, Jean Lorougnon GUEDE University, BP 150 Daloa, Côte d'Ivoire.

activated carbon: banana stalk (Bello et al., 2012), groundnut shell (Malik et al., 2007), oil palm fruit fiber (Tan et al., 2007), cocoa pod husks (Bello and Ahmad, 2011), coconut shell (Das et al., 2015).

Cote d'Ivoire is the largest exporter cocoa in the international market. Annual cocoa production generates a lot of waste consisting of cocoa pod shells. In practice these wastes are usually left in the fields. In order to make better use of this cheap and abundant agricultural waste, it is proposed to convert cocoa pod shells into activated carbon.

The focus of this research was to evaluate the adsorption potential of the cocoa pod shells based activated carbon (CPAC) in removing methylene blue (MB) from aqueous solutions through batch experiments. The equilibrium, kinetic and thermodynamic behaviors of the adsorption process were then evaluated.

Materials And Methods:-

Preparation of activated carbon

The cocoa pods were collected near the city of Daloa (Cote d'Ivoire). They were dried in the oven at 60 °C for 48 h and then ground. The obtained powder underwent successive sieving in order to retain only those whose diameters are included between 0.2 and 0.5 mm.

30 g of cocoa pods powder are impregnated in 300 mL of orthophosphoric acid solution (20%) for 24 h. After 24 h, the sample was then washed in distilled water until the sample was neutralized, filtrated and dried in the oven at 60 °C for 24 h. After drying, the biomass is left at room temperature to cool for at least 30 mn before carbonization. The sample was heated in an electric oven with heating ramps 10 °C per min until 450 °C was maintained for 3 hours. The activated carbon (CPAC) obtained by this treatment were washed with distilled water, filtered and dried at 100 °C for 24 h.

Preparation of the Adsorbate

All the chemicals were used were analytical reagents grade and were prepared in distilled water. Methylene blue (MB) has a molecular weight of 319.85 g/mol, which corresponds to the heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3S$.

Stock solutions of 1000 mg/L of dyes were prepared respectively by dissolving 1.00 g of methylene blue in 1 L of distilled water. The experimental solutions were prepared by diluting a definite volume of the stock solution to get the desired concentration.

Adsorption kinetic studies

For the adsorption kinetic experiments, in 250 mL Erlenmeyer flask, 0.1 g of activated carbon was added to 100 mL of MB solution with an initial concentration of 100 mg/L. The mixtures were agitated at 120 rpm for the allotted contact time (2–100 mn). Activated carbon and solution were separated by centrifuging (SIGMA 2-16P) at 3500 rpm for 10 mn. MB concentration in the solution was measured at 665 nm using UV-visible spectrophotometer (HACH DR 1900).

Equilibrium adsorption studies

The removal of MB by CPAC was investigated under batch conditions. The 250 mL Erlenmeyer flasks were used, the volume of MB was 100 mL, the contact time is 1 h. The agitation was set at 120 rpm.

The effect of the initial dye concentration was investigated at room temperature by varying the initial dye concentration from 20 to 200 mg/L. The mass of activated carbon used is 0.1 g.

The impact of CPAC doses on BM adsorption was explored by reacting different mass of activated carbon (0.05; 0.08; 0.1; 0.2; 0.3; 0.4; 0.5) g with 100 mL of 100 mg/L BM solution.

To study the effect of temperature, four different temperatures (30°C, 40°C, 50°C and 60°C) were applied. Initial dye concentration is 100 mg/L. The mass of CPAC used is 0.1 g.

Adsorption isotherm was studied by varying the MB initial concentration from 50 to 200 mg/L and keeping the adsorbent mass of at 0.1 g. The agitation was set at 120 rpm agitation time for 1h. Experiment was carried out at 3 different temperatures (30 °C, 40°C and 50°C).

The amount of MB adsorbed by the adsorbent and the percentage removal of MB were calculated by using the following equations:

$$q_e = (C_o - C_e) \times \frac{V}{m} \quad (1)$$

$$X (\%) = \frac{C_o - C_t}{C_o} \times 100 \quad (2)$$

Where C_e and C_o (mg/L) are the residual concentration of MB at equilibrium and the initial concentration of MB respectively, V (L) is the solution volume, and m (g) is the mass of CPAC used and X (%) is the percentage of MB removed.

Results And Discussion:-

Effect of contact time and adsorption kinetic

Contact time is an important factor in the adsorption process. It affects the treatment efficiency and also gives an insight into the kinetic of the adsorption. The rate of MB uptake is shown in Fig.1. The rate of adsorption increased rapidly in the first 20 mn, and then it slowed down and reached equilibrium at 60 mn with a maximum rate of 99.68%. The adsorption kinetic of MB on CPAC obtained can be explained by the fact that initially, the adsorption sites are vacant thus easily accessible to MB hence a higher rate of adsorption at the beginning of the reaction. This would be due according to Sakr et al., (2015) to external mass transfer. However, after the initial period, adsorption becomes less; this could be explained by slower diffusion of dissolved species inside the activated carbon pores. Then, appears the equilibrium phase where the adsorbed quantity remains almost constant at this level due to the saturation of active sites (Li et al, 2009).

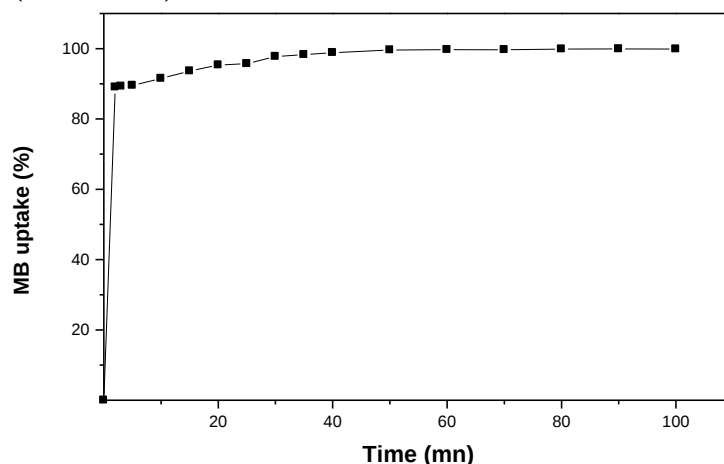


Figure 1:- Effect of contact time on the adsorption of MB on CPAC.

The kinetic studies predict the progress of dyes during the adsorption to reach the equilibrium. In addition, the estimate of the adsorption mechanism is important for design purposes. To analyze the adsorption mechanism of dyes on the activated carbon, pseudo-first order, pseudo-second order, and intraparticle diffusion models were used.

The pseudo-firstorder kinetic model equation is generally expressed as follows (Wang and Li, 2005):

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

where q_e and q_t denote the amount of adsorbed (mg/g) at equilibrium and at any time t , k_1 is the rate constant of pseudo-first order sorption (1/h). the values of constant k_1 and theoretical (q_{cal}) were obtained from the slope and intercept of plots $\ln(q_e - q_t)$ versus time (t) as shown in Fig. 2.

The pseudo-secondorder model based on the adsorption equilibrium capacity may be expressed as the following linear form (Ho and McKay 1999)

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

where k_2 is the rate constant of pseudo-secondorder adsorption (g/(mg·min))

The linear plot of t/q_t versus t determine $1/q_e$ as slope and $1/k_2q_e^2$ as intercept. The linear plot of pseudo-secondorder model is shown in Fig. 2.

In order to gain insight into the mechanisms and rate controlling steps affecting the kinetic of adsorption, the kinetic experimental results were analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism. According to intraparticle diffusion, the uptake varies almost proportionally with the half power of time ($t^{1/2}$). The prediction of the rate-limiting step is essential to have insight into the adsorption mechanism. The intraparticle diffusion coefficient k_d can be calculated by equation (5) (Weber et al., 1963)

$$q_t = k_d \times t^{1/2} + C \quad (5)$$

where k_d is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{1/2}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$ and the intercept of the plot reveals C. The linear plot of intra-particle diffusion model is shown in Fig. 3

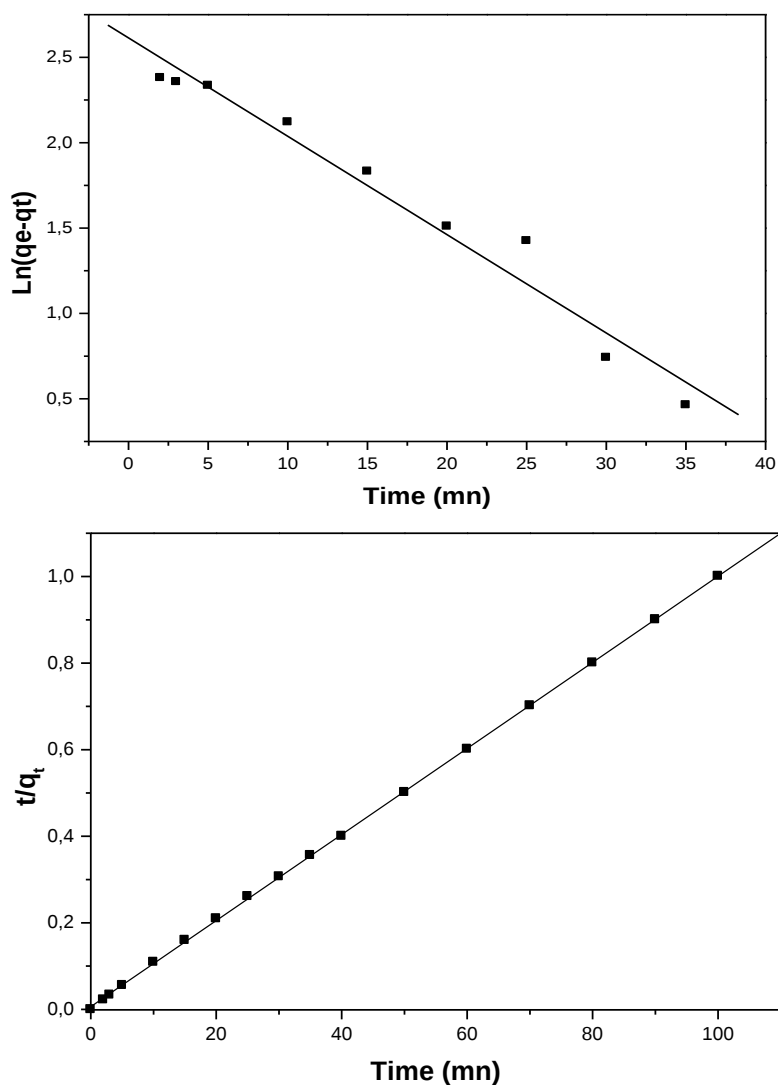


Figure 2:- Pseudo-first-order and Pseudo-second-order kinetic model for BM adsorption onto CPAC.

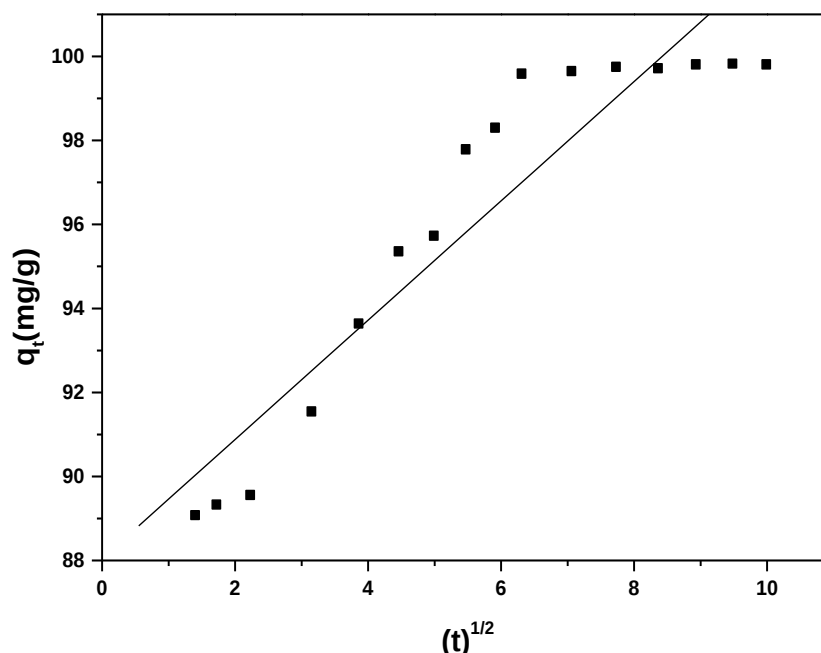


Figure 3:- The intraparticle diffusion kinetic model for BM adsorption onto CPAC.

The experimental and calculated q_e values from the related plots together with the model constants and correlation coefficient R^2 determined from the kinetic models for adsorption of BM onto CPAC are summarized in Table 1. The validity of the exploited models is verified by the experimental $q_{e,exp}$ and correlation coefficient R^2 .

Table 1:- Parameters and correlation coefficient (R^2) of pseudo-first-order, pseudo-second order kinetic model and intra-particle diffusion model for adsorption of MB by CPAC.

Pseudo 1st order				Pseudo 2nd order			intraparticle diffusion		
$q_{e,exp}$	$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	k_2	R^2	C_d	k_d	R^2
(mg/g)	(mg/g)	(1/min)		(mg/g)	(mg/g.min)		(mg/g)		
99.92	68.806	0.066	0.964	101.010	0.012	0.999	87.602	14.70	0.870

The results appear that the model of pseudo-second order was the best for describing the kinetic of BM compared to the other models. The value of correlation coefficients R^2 was superior than 0.99; also the values of ($q_{e,cal}$) calculated from the model of pseudo-second order is approach to the experimental value ($q_{e,exp}$), indicating the applicability of this model to the adsorption of MB on CPAC.

From Fig. 3, the plot is not linear for the whole time interval, indicating that adsorption is affected by several processes. The curve shows three successive linearities: the first could be instantaneous adsorption or adsorption at the external surface of the solid. The second is the gradual adsorption step where intraparticle diffusion is limiting. A third region exists which is the final step before equilibrium where intraparticle diffusion starts to slow down due to the low concentration of the solute in solution. Fig. 3 shows also that the straight line of the linear regression does not pass through the origin ($C_d \neq 0$), which means that intraparticle diffusion is involved in the removal mechanism, but is not the only limiting step.

Batch equilibrium studies

Effect of initial dye concentration

In adsorption processes, the concentration gradient between the adsorbate on the adsorbent and the adsorbate in aqueous phase is the driving force (Ahmad et al., 2014).

The effect of initial dye concentration on the removal of MB by CPAC is shown in Fig.4.

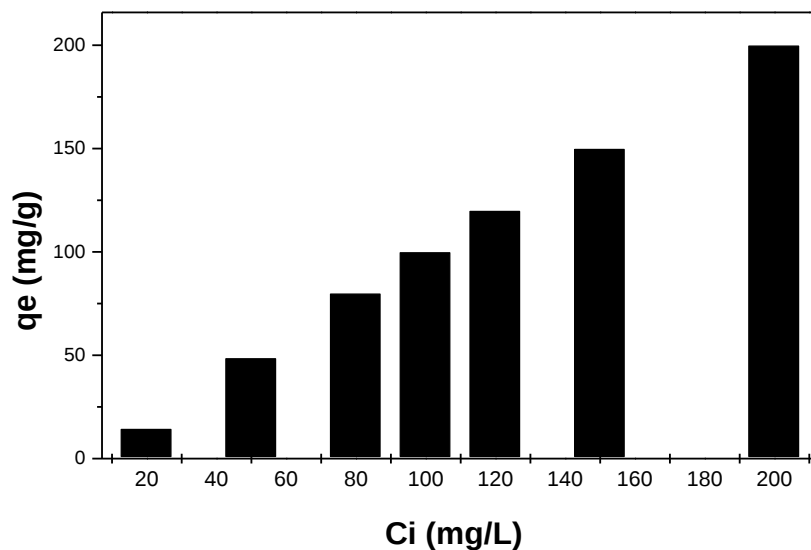


Figure 4:- Effect of initial dye concentration on the amount of MB adsorbed.

The amount of MB uptake increased as the initial concentration increased. This is because with increase in initial concentration, the mass transfer resistance of MB between aqueous and solid phases is reduced by the driving force of the concentration gradient (Akpomie and Dawodu, 2014). Another reason is that an increase in concentration more MB become available for adsorption. According to Jawad et al. (2020), the absence of a saturation level is explained by the fact that the saturation level is not reached and that CPAC could adsorb larger quantities of the dyes.

Effect of Temperature on BM adsorption

In this study, the effect of temperature on the adsorption process was investigated in the range of 30°C – 60°C and the results shown in Fig. 5. It was observed that there was gradual decrease in adsorption capacity of BM as the temperature increases from 30°C to 60°C implying that the process is exothermic. The adsorption capacity of BM was determined as 99.28, 96.36, 95.41 and 94.59 mg/g at 30, 40, 50 and 60°C respectively. The decrease in the amount of BM adsorbed as temperature increased might be attributed to the fact that high temperature causes rupture in the active binding sites of the adsorbent (Aminu and Sulaiman., 2019). This reduces the adsorptive forces between MB and the binding sites resulting in a lower adsorption capacity.

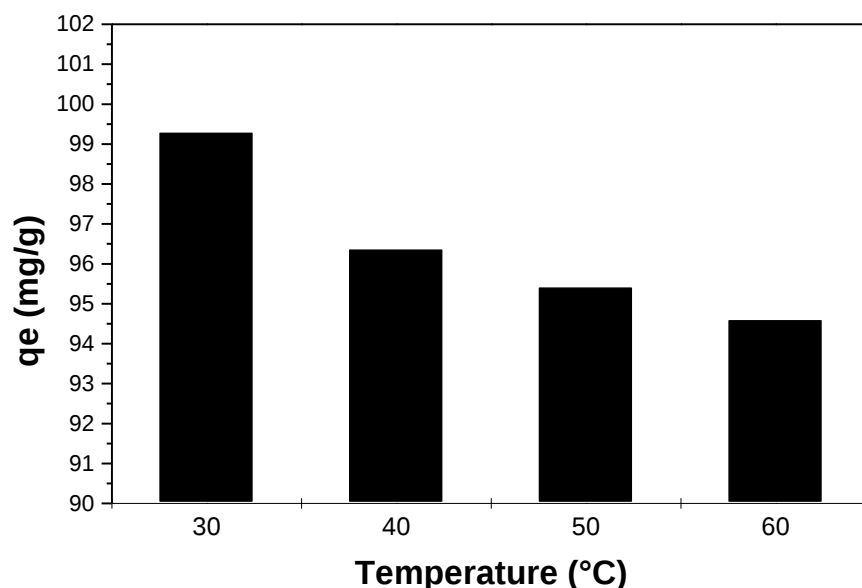


Figure 5:- Effect of temperature on the adsorption of methylene blue from solution.

Adsorption isotherm studies

The adsorption isotherm can describe the distribution of dye between solid phase and the solution at a certain temperature when the equilibrium was reached. Langmuir and Freundlich models were applied to fit the equilibrium data. Each isotherm model was expressed by relative constants which characterized the surface properties and indicated adsorption capacity of the adsorbent used.

Langmuir isotherm is usually applied to monolayer adsorption on homogeneous surfaces with a finite number of adsorption sites. The linear form of Langmuir equation can be expressed as follows (Langmuir, 1918):

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{k_L \times q_{max}} \frac{1}{C_e} \quad (6)$$

where C_e is the equilibrium concentration of MB (mg/L), q_e is the amount of MB adsorbed by a unit mass adsorbent (mg/g), q_{max} represents the maximum amount of MB adsorbed by the unit mass adsorbent (mg/g), and k_L is Langmuir constant (L/mg).

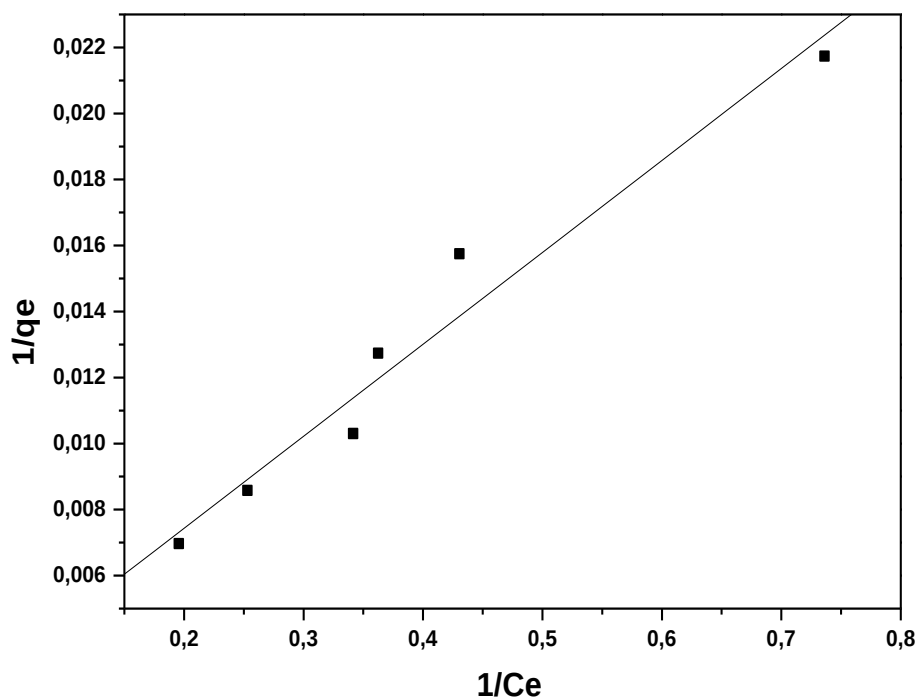
Freundlich isotherm assumes multilayer sorption on a heterogeneous surface. The linear form of Freundlich equation can be expressed as (Freundlich, 1906):

$$\ln q_e = \ln k_F + \left(\frac{1}{n}\right) \ln C_e \quad (7)$$

where q_e and C_e are the same as defined above and k_F and n are Freundlich constants, which indicate the adsorption capacity and adsorption intensity of a given material, respectively. The n values between 1 and 10 indicate favorable adsorption (Bourliva et al., 2013).

Fig. 6 below showed the plots of the linearized Langmuir and Freundlich isotherm for BM adsorption at 30 °C.

(a)



(b)

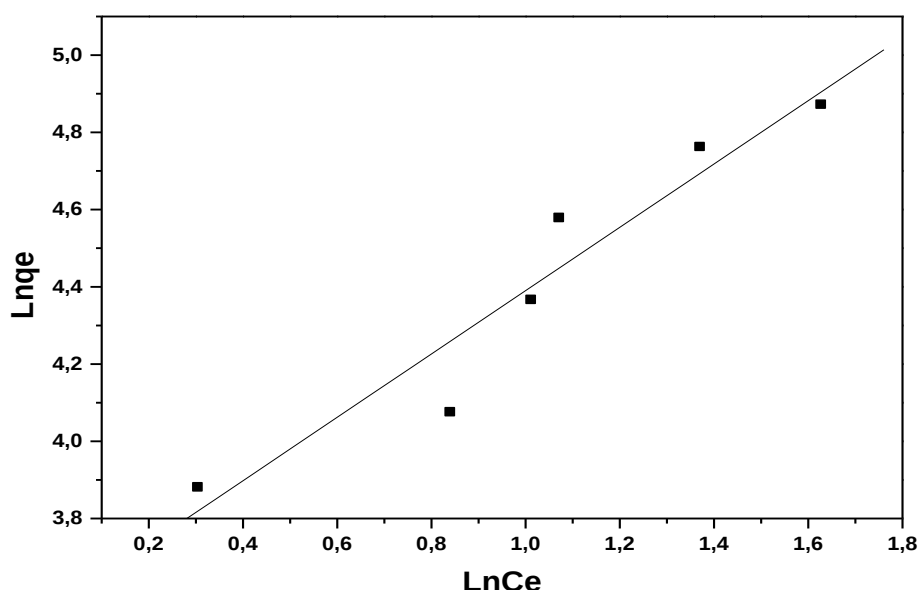


Figure 6:- Langmuir (a) and Freundlich (b) isotherm of BM adsorption onto CPAC at 30 °C.

The fundamental characteristics of Langmuir isotherm have been given by the expression separation factor or equilibrium constant R_L , which is defined by equation (8) as follows:

$$R_L = \frac{1}{1 + (k_L \times C_o)} \quad (8)$$

where C_o is the initial dye concentration and k_L is Langmuir constant. Equilibrium constant R_L signs the nature of adsorption as: (Hameed *et al.*, 2008):

$R_L > 1$ (unfavorable); $0 < R_L < 1$ (favorable); $R_L = 0$ (irreversible); $R_L = 1$ (linear).

Table 2 shows the fitting results of the parameters of the isotherm models at different temperatures

Table 2:- Freundlich and Langmuir isotherms parameters for adsorption of BM onto CPAC at different temperatures.

Isotherms	Parameters	Temperature (°C)		
		30	40	50
Langmuir	q_{max} (mg/g)	526.31	400	384.61
	k_L (L/mg)	0.068	0.051	0.041
	R^2	0.979	0.975	0.998
	R_L	0.129	0.164	0.195
Freundlich	k_F	32.54	22.769	18.722
	$1/n$	0.912	0.788	0.774
	R^2	0.958	0.961	0.985

According to Table 1, the Langmuir isotherm model gives the best fit with the highest R^2 value at all temperatures compared to Freundlich model. The higher correlation coefficients (R^2) of the Langmuir model explain that adsorption process is monolayer and adsorption of each dye molecular has equal activation energy for the binding sites. With the increase of temperature from 30 °C to 50 °C, the maximum capacity at equilibrium of activated carbon decreased from 526.31mg/g to 384.61 mg/g; which implies that the adsorption process is exothermic and favored at lower temperatures. It is also observed that the value of the R_L factor varies from 0.129 to 0.195 when the temperature varies from 30 to 50 °C, which indicates a favourable adsorption, since it is between 0 and 1. The values of $1/n$ ($0.1 < 1/n < 1$) given by Freundlich isotherm confirm a favourable adsorption under the experimental conditions.

Thermodynamic Studies

In understanding better the effect of temperature on the adsorption, it is important to study the thermodynamic parameters such as standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0). The thermodynamic parameters were calculated based on the following equations:

$$\Delta G^0 = -RT \ln k_L = \Delta H^0 - T \Delta S^0 \quad (9)$$

Standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) of adsorption can be estimated from van't Hoff equation given in:

$$\ln k_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (10)$$

where,

T is absolute temperature

R is the gas constant (8.314 J/mol.K),

k_L is adsorption equilibrium constant.

The values of ΔH^0 and ΔS^0 can be determined from the slopes and the intercepts of the linear graph of $\ln(k_L)$ versus $1/T$, as shown in Fig.7.

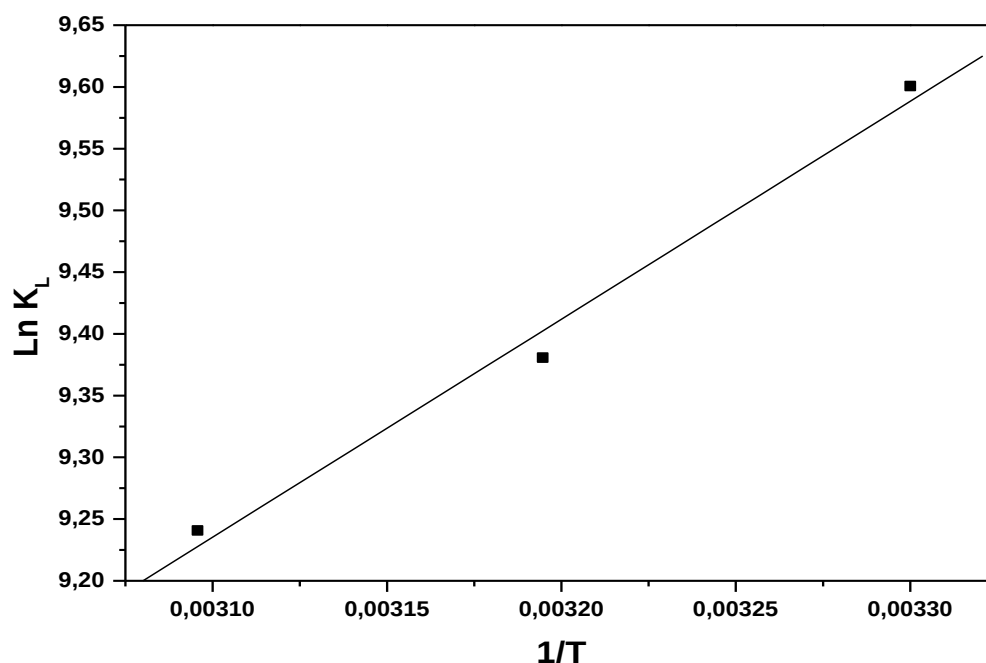


Figure 7:- Plot of $\ln k_L$ versus $1/T$.

The values of thermodynamic parameters at different temperatures are listed in Table 3.

Table 3:- Thermodynamics parameters for methylene blue adsorption on activated carbon.

T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol)	R^2
303	-24.877	-15.849	29.824	0.999
313	-25.204			
323	-25.472			

The negative values of ΔG^0 were indicative of favorable and spontaneous adsorption process. However, the negative values of ΔG^0 decreased with increasing temperature, indicating that the adsorption process is more favorable at low temperatures. (Zhou et al., 2014).

The negative value of ΔH^0 (-15.849 kJ/mol) reveals the exothermic character of the adsorption of MB blue on CPAC. The change in entropy was positive (29.824 J/mol), indicating the entropy of the system increased during the

adsorption; this means that there is an increased disorder at the solid/liquid interface during MB adsorption on CPAC.

Conclusion:-

The feasibility of the agricultural by-product (cocoa pod shell activated carbon) for removing methylene blue from textile wastewater was investigated in this study. The adsorption was found dependent on contact time, temperature and initial concentration of MB. The adsorption equilibrium was best described by the Langmuir isotherm model. The maximum adsorption for MB was found to be 526.31 mg/g at 30 °C. In addition, the MB diffusion in the pores is not the only mechanism limiting the sorption kinetics. Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) showed that the adsorption process of MB was exothermic and spontaneous. The results show that cocoa pod shell activated carbon (CPAC) has the potential to be an effective adsorbent for the removal of methylene blue from an aqueous solution.

References:-

1. Ahmad M. A., Puad N. A. A., Bello O. S. (2014). Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by microwave-induced KOH activation. *Water Res. and Ind.*, 6 :18–35.
2. Akpomie K.G., Dawodu F.A. (2014). Efficient abstraction of nickel(II) and manganese (II) ions from solution onto an alkaline-modified montmorillonite. *J. of Taibah Univ. for Sci.*, 8: 343–356.
3. Aljeboree A. M., Alshirifi A. N., Alkaim A. F. (2017). Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon. *Arabian J. of Chem.*, 10: 3381-3393.
4. Aminu I., Sulaiman M.S. (2019). Equilibrium, Kinetics and Thermodynamic Studies of Adsorption of Cadmium(II) Ions onto Activated Carbon from African Elemi Seeds. *Amer. J. of Environ. Eng.*, 9(1): 17.
5. Beluci N.D.C.L., Mateus G.A.P., Miyashiro C.S., (2019). Hybrid treatment of coagulation/flocculation process followed by ultrafiltration in TiO₂-modified membranes to improve the removal of reactive black 5 dye. *Sci Total Environ.*, 664: 222–229.
6. Bello O.S., Ahmad M. A. (2011). Adsorptive removal of a synthetic textile dye using cocoa pod husks. *Toxicol. and Environ. Chem.* 93 (7):1298-1308.
7. Bello O.S., Ahmad M.A., Ahmad N. (2012). Adsorptive features of banana (*Musa paradisiaca*) stalk-based activated carbon for malachite green dye removal. *Chem. Ecol.* 28: 153–167.
8. Bello O. S., Adegoke K. A., Sarumi O. Lameed O.S (2019). Functionalized locust bean pod (*Parkia biglobosa*) activated carbon for Rhodamine B dye removal. *Heliyon* 5:
9. Bourliva A., Michailidis K., Sikilidis C., Filippidis A., Betsiou M., (2013). Lead removal from aqueous solutions by natural Greek bentonites,” *Clay Minerals*, 48 (5): 771–787.
10. Das D., Samal D.P., Meikap BC (2015). Preparation of Activated Carbon from Green Coconut Shell and its Characterization. *J Chem Eng Process Technol* 6 (5): 1–7.
11. Freundlich H., (1906). Over the adsorption in solution. *J. of Phys. Chem.*, 57: 384-470.
12. Hameed B.H., Chin L.H., Rengaraj S. (2008) Adsorption of 4-chlorophenol onto activated carbon prepared from rattan sawdust. *Desalination* 225 (1–3): 185–198.
13. Ho YS, McKay G (1999). Pseudo-second-order model for sorption processes. *Process Biochem* 34 (5): 451–465.
14. Jawad A.H., Alkarkhi A.F.M., Mubarak NSA. (2015). Photocatalytic decolorization of methylene blue by an immobilized TiO₂ film under visible light irradiation: optimization using response surface methodology (RSM). *Desalin. Water Treat.*, 56:161–172.
15. Jawad A.H., Abdulhameed A. S., Mastuli M.S. (2020). Acid-fractionalized biomass material for methylene blue dye removal: a comprehensive adsorption and mechanism study. *J. of Taibah University for Sci.*, 14 (1): 305–313.
16. Langmuir I., (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *J. of the American Chem. Society* 40 (9): 1361–1403.
17. Li K., Zheng Z., Huang X., Zhao G., Feng J., Zhang J. (2009). Equilibrium, Kinetics and Thermodynamic Studies on the adsorption of 2-nitroaniline onto activated carbon prepared from cotton stalk fibre. *J. Hazard. Mater* 166: 213-220.
18. Malik R., Ramteke D.S., Wate S.R. (2007). Adsorption of malachite green on groundnut shell waste based powdered activated carbon. *Waste management* 27 (9): 1129-1138.

19. Nidheesh P.V., Zhou M., Oturan M.A. (2018). An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes. *Chemosphere*. 197 : 210–227.
20. Sakr F., Sennaoui A., Elouardi M., Tamimi M., Assabbane A. (2015). Etude de l'adsorption du Bleu de Méthylène sur un biomatériau à base de Cactus. *J. of materand Environ.Sci*. 6 (2): 397– 406.
21. Tan I.A.W., Hameed B.H., Ahmad A.L. (2007). Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. *Chem. Eng. J.*, 127: 111–119.
22. Wang S., Li H., (2005). Dye adsorption on unburned carbon: kinetics and equilibrium. *J. of Hazard Mater*, 126 (1): 71–77.
23. Weber WJ, Morris J.C., Sanit J. (1963). Kinetics of adsorption on carbon from solution. *J.of the Sanitary Eng. Division* 89: 31–59.
24. Zhou Z., Lin S., Yue T., Lee T.C. (2014). Adsorption of food dyes from aqueous solution by glutaraldehyde cross-linked magnetic chitosan nanoparticles. *J. of Food Eng.* 126: 33-141.