

ISOTHERMS, KINETICS AND THERMODYNAMICS OF METHYLENE BLUE ADSORPTION ON ACTIVE CARBON FROM POLYFURFURYL ALCOHOL

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ABSTRACT

This study investigates the isotherm and kinetics of adsorption of methylene blue (MB) from aqueous system on polyfurfuryl alcohol carbon (PFAC). Experimental parameters like initial concentration of MB (1-3 mg/50 mL), reaction time (0-60 min.) and temperature (302-328 K) were studied for the adsorption process using isotherms, adsorption kinetics and thermodynamics. The results obtained show that adsorption of MB on PFAC fits both the Langmuir and Freundlich isotherms well but the Langmuir model explains the adsorption equilibrium data better. The experimental adsorption capacity of this active carbon for MB was 23.80 mg/g, equivalent to specific surface area 88.34 m²/g. The calculated thermodynamic values: ΔH° (– 9.0 kJ/mol.), ΔS° (– 19.20 J/mol.) and E_a (– 3.60 J/mol.), indicate exothermic and physical nature of adsorption as well as decreased randomness at the adsorbate-adsorbent interface. The sticking probability (ξ°) value (0.55) show that the probability of MB molecules to stick on the surface of this active carbon is high. The negative ΔG° values (– 5.78 to – 6.28 kJ/mol.K) at 302–328 K, confirms a spontaneous adsorption process dominated by physisorption. Adsorption of MB on PFAC was predominantly governed by pseudo-second order kinetics. This active carbon from polyfurfuryl alcohol shows potential for the removal of organic pollutants like MB from aqueous systems.

Keywords: Polyfrufuryl Alcohol, Active Carbon, Methylene Blue, Adsorption, Isotherms, Kinetics, Thermodynamics.

INTRODUCTION

One of the less energy-intensive process unit operations in industries, known as an efficient method for the removal of organic dyes from aqueous medium, is the adsorption process¹. To be able to improve on the efficiency of the adsorption process, general understanding of the interaction between organic solutes and porous solids is unavoidable. This makes the study of adsorption of Methylene blue (methylthioninium chloride) from aqueous medium by active carbons important.

Methylene blue (MB) is classified as an organic cationic dye, a group of dyes considered to be very toxic – more toxic than anionic dyes^{2,3}. It is widely used in dyeing of

materials like hemp, silk fabric, stained paper; coloring of bamboo and wood, and as a chemical agent in printing and dyeing enterprises³. It is also used in the treatment of methemoglobinemia and urinary tract infections. MB also has photodynamic antimicrobial applications. Wastewaters containing MB usually have high concentration and color depth, hence, a major source of pollution¹.

The cosmetic, detergent, food, paper, pharmaceutical, photography, plastic, soap and textile industries use a variety of types of dye stuff. Production processes of these industries, especially the detergent, soap and textile industries, require large volumes of

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water. As a result, these industries are leaders in terms of volume of colored wastewaters discharged into the environment. When such wastewaters empty into bodies of surface water, they impede light penetration of the ecosystem and hinder the process of photosynthesis that supports life in the system.

The aim of this study is to investigate the nature of adsorption, kinetics and thermodynamics of MB on an active carbon from polyfurfuryl alcohol.

MATERIALS AND METHODS

Materials' Collection and Preparation

Collection and preparation of furfuryl alcohol and polyfurfuryl alcohol were as reported in an earlier publication⁴.

Preparation of Active Carbons

The polyfurfuryl alcohol carbon (PFAC) was prepared as reported in an earlier publication⁴.

Methylene Blue Adsorption

This was carried out as reported in an earlier publication⁴. Sample (100 mg) of PFAC was dispersed into a 250-mL Erlenmeyer flask. MB solution (50 mL) of varying concentrations (1.0, 2.0 and 3.0 mg) was added and stoppered. The flask was shaken for various contact times (5, 10, 15, 20, 25, 35 and 60 min. respectively) at room temperature of 302 K (29 °C). The mixture in the flask was centrifuged for 5 min. and analyzed using Cole 7506 UV-VIS spectrophotometer at 665 nm wavelength. This was repeated at different temperatures (308, 318 and 328 K) for various contact times (5, 10, 15, 20, 25 and 30 min.) using the 2.0 mg MB solution. Standard solutions of MB were used for calibration.

RESULTS AND DISCUSSION

Itodo⁵ reported the application of methylene blue (MB) and iodine adsorption in surface area measurement for liquid phase adsorption. The specific surface area of the adsorbent can

be estimated by equation (1) using MB adsorption and has direct proportionality with adsorption efficiency.

$$S_{MB} = \frac{Q_o \times a_{MB} \times N \times 10^{-3}}{M} \quad (1)$$

where S_{MB} = specific surface area (m^2g^{-1}), Q_o = maximum monolayer coverage i.e. equilibrium amount (mgg^{-1}) of MB adsorbed on adsorbent, a_{MB} = the occupied surface area of one molecule of MB = $197.2 \text{ \AA}^2 = 1.972 \times 10^{-18} \text{ m}^2$, N = Avogadro's number = $6.02 \times 10^{23} \text{ mol}^{-1}$ and M = molecular weight of MB = 319.9 gmol^{-1} . Total surface area of the adsorbent is indicated by the iodine number, typically 500 – 1200 mgg^{-1} , equivalent⁵ to surface area 900 – 1100 m^2g^{-1} .

Using equation (1), the specific surface area for PFAC was calculated to be 88.34 m^2/g .

Adsorption Isotherms

Langmuir Isotherm

Langmuir isotherm is one of the most commonly studied isotherm models that describes the correlation between the amounts (mg/g) of adsorbate adsorbed on the adsorbent and the adsorbate concentration (mg/L) in solution at equilibrium condition. The model feigns that at equilibrium, monolayer adsorption of adsorbate occurs at established number of homogeneously distributed adsorption sites over the adsorbent surface, and these sites have equal attraction for the adsorbate molecules. The linear form of the Langmuir isotherm model is expressed as⁶

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o} \quad (2)$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbate adsorbed on the adsorbent at equilibrium, b is the Langmuir isotherm constant (L/mg) and Q_o is the maximum monolayer coverage capacity (mg/g) i.e. adsorption capacity of the adsorbent. A straight-line plot of C_e/q_e against C_e gives a slope of $1/Q_o$ and an intercept equal to $1/bQ_o$. The constant b corresponds to attraction of the adsorbate for

the adsorbent and relates a dimensionless constant called separation factor (R_L) expressed as

$$R_L = \frac{1}{1 + bC_o} \quad (3)$$

where C_o is the initial concentration of adsorbate (mg/L). The R_L value is an indication of the nature of adsorption⁶ as either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Freundlich Isotherm

Freundlich isotherm demonstrates that the adsorption process on a heterogeneous adsorbent surface is multilayered, and the adsorption sites have varying degrees of attraction for the adsorbate. The linear form of the Freundlich isotherm model is expressed as^{1,7}

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where K_F is Freundlich isotherm constant (mg/g or dm³/g) associated with adsorbent adsorption capacity and n is the adsorption intensity related to the heterogeneity of the adsorbent surface. A plot of $\log q_e$ against $\log C_e$ gives a straight-line of slope $1/n$ and an intercept equal to $\log K_F$. Favorable adsorption is typically indicated⁸ by a Freundlich constant (n) of between 1 and 10. $n = 1$ points towards a linear adsorption process with uniform (constant) energy across the entire adsorbent surface such that the binding strength is increased as more adsorbate binds⁹.

Fig. 1 presents Langmuir isotherms for PFAC in different concentrations of MB solution; all showing a very good fit (average $R^2 = 0.996$). Table 1 shows that all the Langmuir parameters are influenced by the initial adsorbate concentration. The adsorption capacity i.e. the maximum monolayer coverage capacity (Q_o) of PFAC increased with initial concentration of MB. This suggests the maximum monolayer coverage capacity of porous materials is dependent on initial adsorbate concentration. This

observation is consistent with that reported¹⁰⁻¹² for other precursors and it's responsible for the time taken by sorption processes to attain equilibrium position. The stronger the dependency, the shorter the time taken for attainment of equilibrium position.

Table 1: Langmuir and Freundlich Isotherm Parameters for MB Adsorption on Active PFA Carbon at 302 K

Isotherm Parameters	MB Concentration (mg/50 mL)		
	1.0	2.0	3.0
Langmuir Isotherm:			
Evaluated Capacity, Q_o , (mg/g)	3.98	10.63	13.93
Experimental Q_o , (mg/g)	7.60	16.50	23.80
Langmuir Constant, b , (L/mg)	0.42	0.38	0.19
Separation Factor, R_L	0.11	0.06	0.08
Correlation Coefficient, R^2	0.995	0.997	0.997
Freundlich Isotherm:			
Evaluated Capacity, K_F , (mg/g)	19.11	32.67	71.71
Experimental K_F , (mg/g)	7.60	16.50	23.80
Freundlich Constant, n	1.75	2.90	2.31
Correlation Coefficient, R^2	0.975	0.966	0.988

The Langmuir constant, b (a measure of attraction of the MB molecules to the PFAC surface), is also influenced by the initial concentration of MB. From Table 1, the attraction of MB molecules for PFAC decreases with increase in its initial concentration. This could be attributed to the surface functional groups of the active carbon and protonation as well as concentration-dependent conversions (e.g. formation of dimers and high-order aggregates) associated with the MB molecule.

The evaluated separation factor R_L , indicative of nature of adsorption, was $0 < R_L < 1$ (Table 1); indicating that the adsorption of MB on PFAC is favorable. This factor was also observed to be initial adsorbate-concentration dependent. The low R_L values suggests that the interaction between the MB molecules and PFAC surface functional groups is relatively strong¹³ and the strength increases with initial MB concentration.

The Freundlich isotherm (Fig. 2) gave straight-line plots (average $R^2 = 0.976$) for the different initial concentrations of MB. The correlation coefficients for the Langmuir isotherms are higher than that for the Freundlich isotherms. Thus, the data fits the Langmuir model better than the Freundlich model. Parameters evaluated from the Freundlich isotherm (Table 1) show that the Freundlich equilibrium constant (K_F), related to adsorption capacity and intensity of PFAC, is MB initial-concentration dependent. The K_F values increased with initial concentration of MB, and compare poorly with the experimental values. This is expected since the Freundlich model doesn't predict a

maximum capacity for the adsorbent. The, n values are $1 < n < 3$, which indicates favorable adsorption process and imply strong interaction between MB molecules and PFAC surface. These values meet the heterogeneity condition $1 < n < 10$ ($0 < 1/n < 1$) as required by the model, suggesting a heterogeneous adsorption scenario.

On the whole, these results show that the Langmuir model explains the adsorption equilibrium data for MB on PFAC better than the Freundlich model. From the values of correlation factors, Fig.3 seems to suggest that this position is emphasized as the system temperature increases.

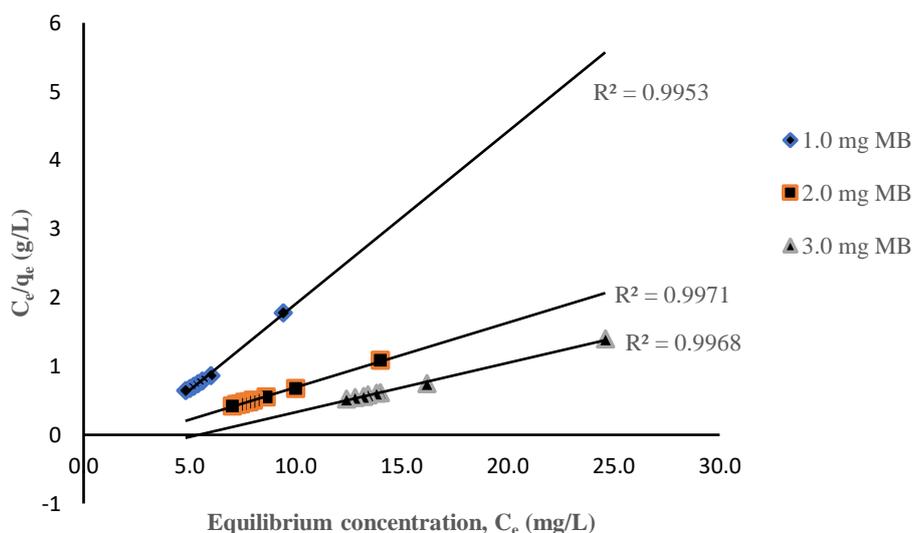


Figure 1: Langmuir Isotherms for Adsorption of MB Solutions on PFAC at 302 K

Frumkin isotherm

The Frumkin isotherm asserts that adsorbed molecules do interact and affect further adsorption by either repulsion or attraction of molecules. It is generally expressed in a linear form as¹⁴

$$[\theta/(1 - \theta)]\exp(-2\alpha\theta) = KC_e \quad (5)$$

where the term α describes molecular interactions in the adsorbed adsorbate layer and the heterogeneous nature of the surface; and can take either positive or negative values. Positive values of α suggests that interactions between molecules are attractive

in nature and give rise to increase in the adsorption energy with increased surface coverage (θ).

Rearrangement of equation (5) could take any of the linear forms:

$$\ln[(\theta/(1 - \theta))/C_e] = \ln K + 2\alpha\theta \quad (6)$$

or

$$\log[(\theta/(1 - \theta))/C_e] = \log K + \frac{2\alpha\theta}{2.303} \quad (7)$$

Where the Frumkin isotherm is applicable, a plot of $\log[(\theta/(1 - \theta))/C_e]$ against θ would

give a straight line from which α and K could be evaluated from the slope and intercept respectively.

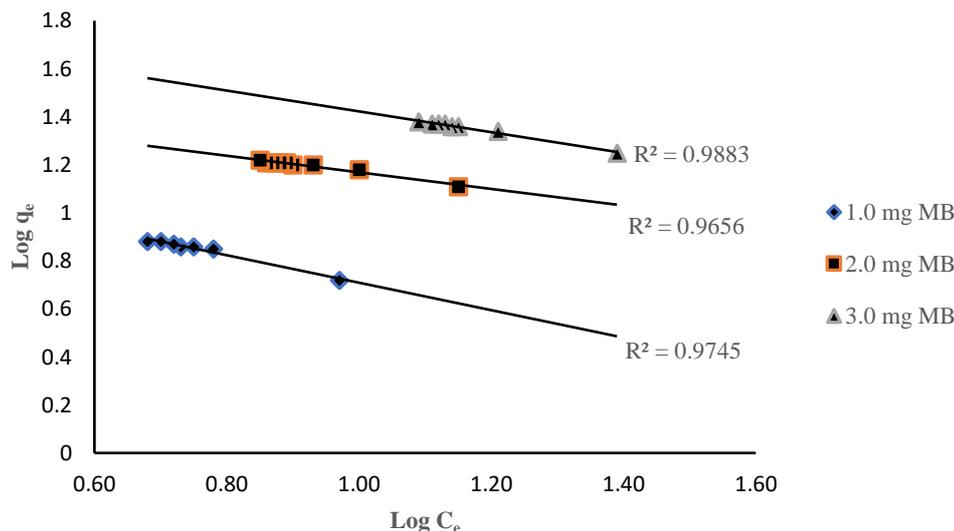


Figure 2: Freundlich Isotherms for Adsorption of MB Solutions on PFAC at 302 K

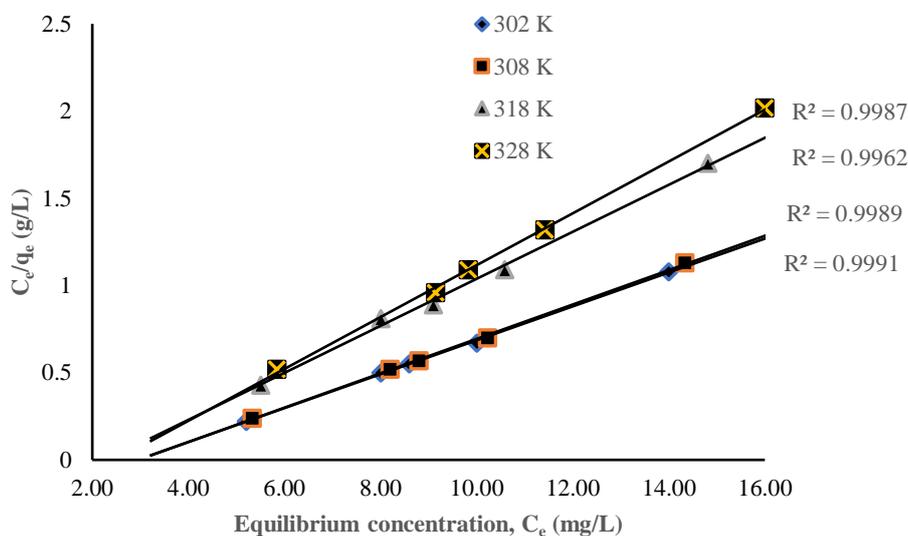


Figure 3: Langmuir Isotherms for Adsorption of 2 mg MB Solution on PFAC at 302-328 K

The Frumkin isotherm (Fig. 4) shows an excellent fit ($R^2 \cong 1.0$) of the adsorption equilibrium data for MB adsorption on PFAC. This implies that one adsorbed molecule of water is replaced by a molecule of MB (i.e. $x = 1/y \cong 1$). The calculated value of the lateral molecular interaction parameter (α) is a positive appreciable value (15.65). This implies substantial increase in adsorption energy takes place with increase in surface

coverage. It also means significant intermolecular interaction (attraction) between adsorbed MB molecules.

Flory-Huggins isotherm

Flory-Huggins isotherm expresses the degree of surface coverage physiognomies of the adsorbate on the adsorbent¹⁵. Its linear form is generally expressed as¹⁴:

$$\theta/x(1 - \theta)^x = KC_e \quad (8)$$

where x is a size parameter and measures the substituted number of adsorbed water molecules i.e. number of active sites. The linear form of this isotherm is

$$\log(\theta/C_e) = \log xK + x \log(1 - \theta) \quad (9)$$

A plot of $\log(\theta/C_e)$ against $\log(1 - \theta)$ gives a straight line with slope equal to x and an intercept equal to $\log xK$, if Flory-Huggins isotherm is obeyed.

Fig. 5 presents Flory-Huggins isotherm with an excellent fit ($R^2 = 1.0$) for MB adsorption on PFAC, using equation (9). The value of x , number of water molecules replaced by a single MB molecule at the surface of PFAC, is $0.09 \approx 0.1$ (Table 2). This value is lower than the 0.87 predicted by the kinetic model, indicating that crowded conditions exist due to both geometric and steric factors¹⁴.

El-Awady isotherm

This is a kinetic-thermodynamic model. The kinetic perspective presents the adsorption process¹⁴ as occupation of $1/y$ number of surface active sites by the adsorbate molecules according to equation (10):



where y is the number of adsorbate molecules occupying one active site on the adsorbent surface. From this perspective, equation (8) takes the form:

$$\theta/(1 - \theta) = K'(C_e)^y \quad (11)$$

or

$$\log[\theta/(1 - \theta)] = \log K' + y \log C_e \quad (12)$$

where

$$K = K' (1/y) \quad (13)$$

These equations (11 & 12) are forms of El-Awady adsorption isotherm^{14,16}. Where this isotherm fits, a plot of $\log[\theta/(1 - \theta)]$ versus $\log C_e$ gives a straight line with slope equal to x and intercept $\log K'$. Values of $y > 1$ suggests formation of multilayers of

adsorbate on the adsorbent surface while $y < 1$ implies a given adsorbate molecule occupies more than one active site^{14,16}.

Fig. 6 presents the isotherm for the El-Awady model for MB adsorption on PFAC. Again, an excellent fit ($R^2 = 0.9993 \approx 1.0$) was obtained for the adsorption equilibrium data for MB adsorption on PFAC. Evaluated parameters for the Frumkin, Flory-Huggins and El-Awady isotherms were as presented in Table 2. The y value, 1.16, suggests multilayer adsorption of MB molecules on the PFAC surface. The calculated number of active sites ($1/y$) was 0.87. The fractional $1/y$ value has physical interpretation and suggests varying degrees of activity at the sites, including the adsorbed MB molecule making it more or less difficult for another molecule to be adsorbed. It could also have a chemical interpretation suggestive of a change in geometry (isomerism) of the MB molecule as a result of changes in system parameters (concentration, pH, temperature, etc.).

Kinetics of Adsorption

Generally, the study of kinetic models enables understanding of the adsorbent-adsorbate interactions, i.e. the rate of adsorbate removal by an adsorbent with respect to equilibrium time.

Pseudo-First Order Model

Pseudo-first order kinetic model is generally expressed as^{16,17}

$$\frac{dq_t}{dt} = k(q_e - q_t) \quad (14)$$

where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and time t (min.) respectively and k (min.^{-1}) is the pseudo-first order rate constant. Within the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = t$ at $t = t$, the linear integrated form of equation (14) is

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303} t \quad (15)$$

This equation (15) has been commonly used to describe adsorption of pollutants from aqueous media. In most cases in the literature, this pseudo-first order equation does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 30

minutes of the adsorption process¹⁸. This is the kinetics of adsorption study in the regions with constant adsorption acceleration (KASRA) model¹⁹ and was employed in this study for the application of equation (15).

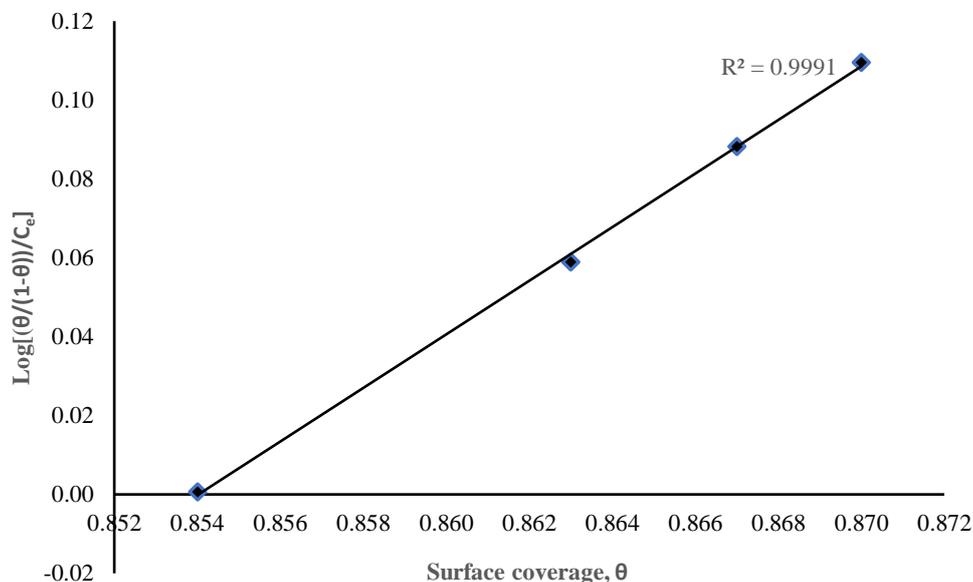


Figure 4: Frumkin Isotherm for Adsorption of 2 mg MB Solution on PFAC at 302-328 K

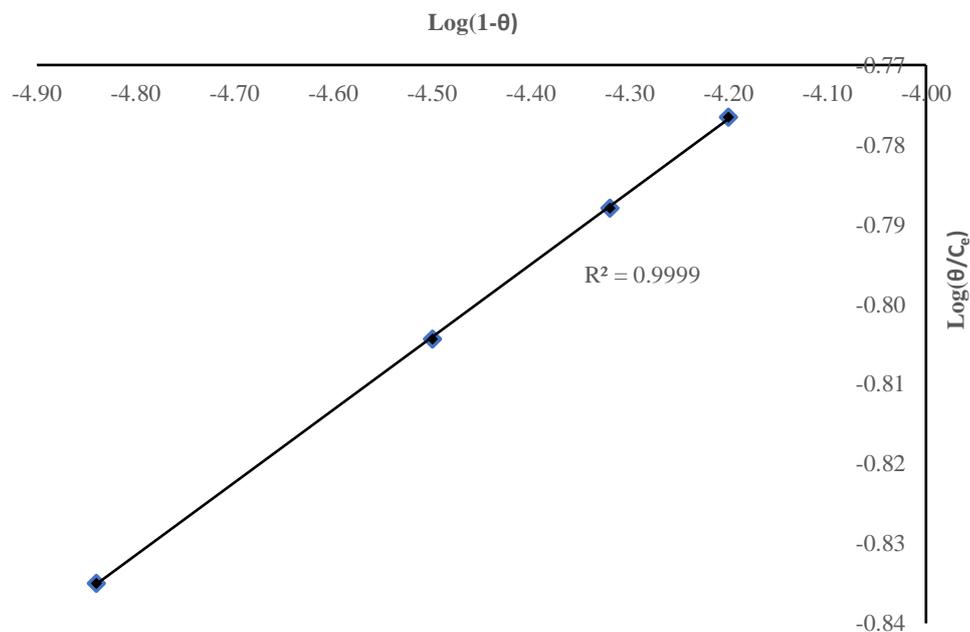


Figure 5: Flory-Huggins Isotherm for Adsorption of 2 mg MB Solution on PFAC at 302-328 K

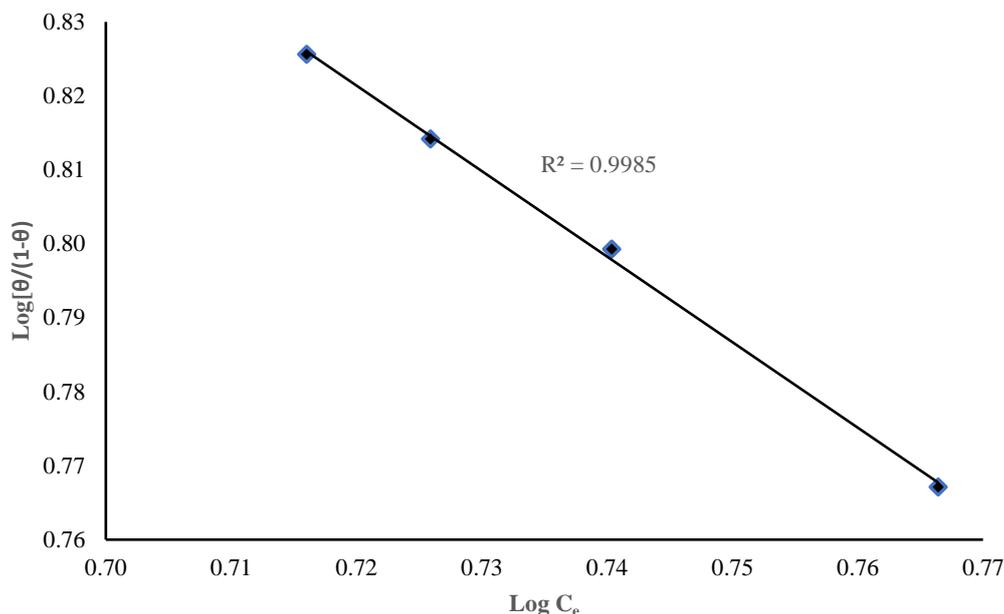


Figure 6: El-Awady Isotherm for Adsorption of 2 mg MB Solution on PFAC at 302-328 K

Pseudo-Second Order Model

The pseudo-second order kinetics is commonly presented as^{17,18}

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (16)$$

where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and time t (min.) respectively and k (mg/g min.) is the pseudo-second order rate constant. Within the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = t$ at $t = t$, the linear integrated form of equation (15) could be expressed in any of the forms below:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (17)$$

or

$$\frac{t}{q_t} = \frac{1}{\nu} + \frac{1}{q_e}t \quad (18)$$

where $\nu = kq_e^2$ can be regarded as the initial adsorption rate as $t/q_t \rightarrow 0$. If pseudo-second order kinetics applies, a plot of t/q_t against t of equation (18) gives a linear relationship, from which q_e , k and ν are determined.

The linear plots of the pseudo-first order and pseudo-second order presented in Figs. 7 & 8 respectively, indicate that the experimental data is, generally, better described by the pseudo-second order model (average $R^2 = 0.997$) than the pseudo-first order model (average $R^2 = 0.982$). The experimental and calculated equilibrium adsorption capacities (Table 3) show that the q_e values for PFAC evaluated through pseudo-second order kinetics were, by-and-large, closer to the experimental values than those calculated using the pseudo-first order kinetics. The pseudo-first order adsorption rate constant (k) values present a non-steady decrease with increase in initial concentration of MB while values for the pseudo-second order rate constant decreased steadily with increase in concentration of MB. The foregoing observations suggests that the pseudo-second order kinetic model provides a better fit for the removal of MB from aqueous systems using PFAC.

Thermodynamics of Adsorption

The nature of an adsorption process is confirmed by the evaluation of its thermodynamic parameters. Thermodyna -

mic parameters like free energy change (ΔG_{ads}), enthalpy change (ΔH_{ads}) and entropy change (ΔS_{ads}) of adsorption are calculated to evaluate the feasibility and spontaneity of the process. The free energy of adsorption (ΔG_{ads}) is related to the adsorptive equilibrium constant, K_{ads} , (L/mol.) expressed in equation (2) as:

$$K_{ads} = bQ_o \quad (19)$$

where Q_o is the maximum Langmuir adsorption capacity of the adsorbent and b is Langmuir isotherm constant. The standard free energy change of adsorption:

$$\Delta G_{ads}^o = -2.303RT \log(K_{ads}) \quad (20)$$

is then expressed as:

$$\Delta G_{ads}^o = -2.303RT \log(bQ_o) \quad (21)$$

where R is the gas constant and T is the thermodynamic temperature. Negative values of ΔG_{ads}^o are usually characteristic of spontaneity of the adsorption process. Generally, values of ΔG_{ads}^o up to -20 kJmol^{-1} are consistent with the electrostatic interaction between the charged adsorbate species and the adsorbent surface (physisorption) while

ΔG_{ads}^o values around -40 kJmol^{-1} or less are associated with chemisorption as a result of sharing

Table 2: Frumkin, Flory-Huggins and El-Awady Parameters for MB Adsorption on Active PFAC at 302-328 K

Isotherms/ Parameters	PFAC
<i>Frumkin:</i>	
α	15.65
K	1.58×10^{-6}
R^2	1.000
<i>Flory-Huggins:</i>	
x	0.09
K	4.43
R^2	1.000
<i>El-Awady:</i>	
y	1.16
$1/y$	0.87
K	11.89
R^2	0.999

or transfer of electrons from the adsorbate species to the adsorbent surface to form a coordinate type of bond^{20,21}. The Van't-Hoff expression:

$$\log(K_{ads}) = \frac{1}{2.303} \left(\frac{\Delta S_{ads}^o}{R} - \frac{\Delta H_{ads}^o}{RT} \right) \quad (22)$$

is commonly used to evaluate the standard enthalpy (ΔH_{ads}^o) and standard entropy change (ΔS_{ads}^o) of the adsorption process.

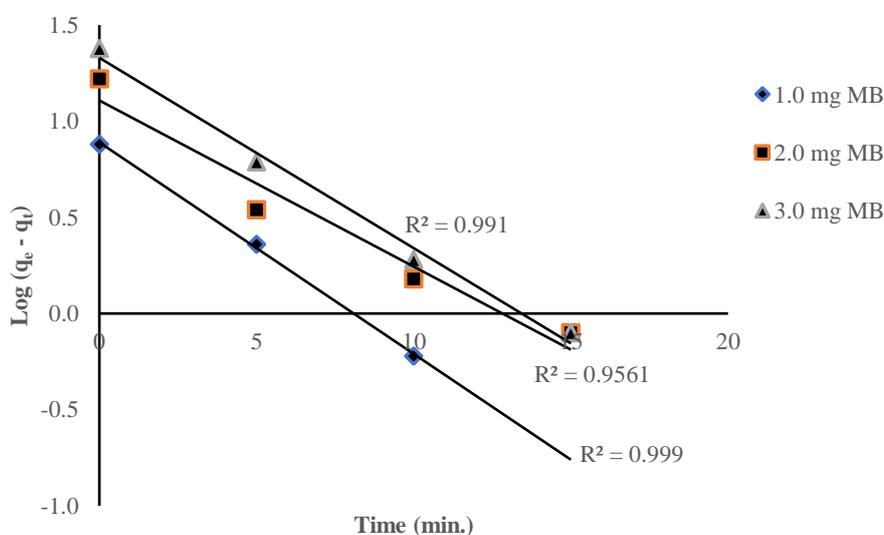


Figure 7: Pseudo-First Order Kinetics for Adsorption of MB Solutions on PFAC at 302 K

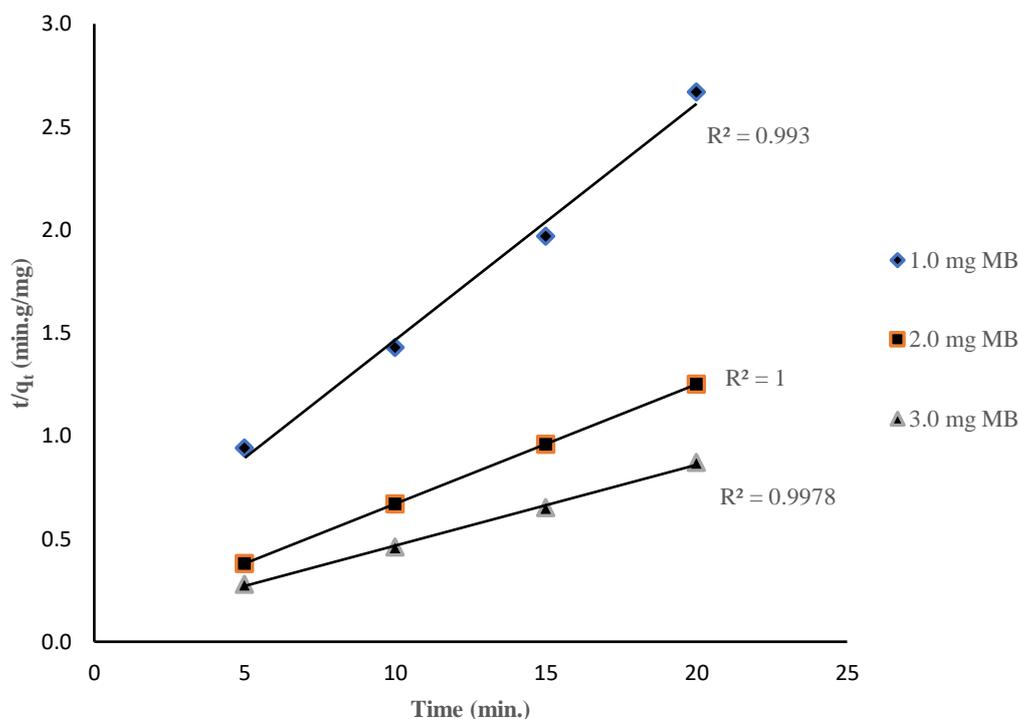


Figure 8: Pseudo-Second Order Kinetics for Adsorption of MB Solutions on PFAC at 302 K

Table 3: Pseudo-First Order Kinetics and Pseudo-Second Order Kinetics Parameters for MB Adsorption on Active PFA Carbon at 302 K

Isotherm Parameters	MB Concentration (mg/50 mL)		
	1.0	2.0	3.0
Experimental q_e (mg/g)	7.60	16.50	23.80
<i>Pseudo-First Order Kinetics:</i>			
Equilibrium Adsorption Capacity, q_e , (mg/g)	7.76	12.82	21.38
Rate Constant, k , x 10^{-1} (min. ⁻¹)	2.53	2.00	2.28
Correlation Coefficient, R^2	0.999	0.956	0.991
<i>Pseudo-Second Order Kinetics:</i>			
Equilibrium Adsorption Capacity, q_e , (mg/g)	8.59	17.24	25.51
Rate Constant, k , x 10^{-2} (g/mg min.)	4.23	3.74	2.05
Initial Rate, v (mg/g min.)	3.13	11.11	13.33
Correlation Coefficient, R^2	0.993	1.000	0.998

From the linear regression equation of the van't-Hoff plot of $\log(K_{ads})$ versus $1/T$, values of ΔH_{ads}^0 and ΔS_{ads}^0 are obtained from the slope and the intercept respectively. The thermodynamic parameters (ΔG_{ads} , ΔH_{ads} and ΔS_{ads}) of the adsorption process at different temperatures were evaluate using equations (19)-(22) and Fig. 9.

Activation Energy of Adsorption

The modified Arrhenius-type equation¹⁸ related to surface coverage (θ):

$$\theta = \frac{C_o - C_e}{C_o} \quad (23)$$

is commonly employed in the evaluation of the activation energy of adsorbate adsorption (E_{ads}) and sticking probability (ξ^o) onto the adsorbent.

Sticking probability is the likelihood that molecules are entrapped on surfaces and adsorbed. It is dependent on the adsorbate-adsorbent system under study and its linear form is expressed as,

$$\ln(1 - \theta) = \ln \xi^o + \frac{E_{ads}}{RT} \quad (24)$$

or

$$\log(1 - \theta) = \log \xi^o + \frac{E_{ads}}{2.303RT} \quad (25)$$

where R is the universal gas constant and T is the thermodynamic temperature. A plot of $\log(1 - \theta)$ versus $1/T$ gives a straight line and enables the evaluation of E_{ads} and ξ^o (Fig. 10).

Table 4 presents a summary of the thermodynamic and thermodynamic-related parameters determined in this work. The results show that the adsorption capacity of PFAC decreased with increase in temperature within the temperature range 302 – 328 K. This suggests, the MB adsorption process on active PFAC is exothermic within this temperature range. Table 4 shows a negative value (-9.00 kJ/mol.) for standard enthalpy of adsorption (ΔH_{ads}^o) of MB. This collaborates the exothermic nature of MB adsorption on this active carbon suggested by decrease in adsorption capacity with increase in temperature. According to Myina *et al.*¹², Gupta²², Bharat and Debajyoti²³ and, if $\Delta H^o < 25.0$ kJ/mol., the sorption is physical (physisorption) whereas $\Delta H^o > 40.0$ kJ/mol. suggests chemisorption. Thus, from the standard enthalpy of adsorption of MB obtained for PFAC, the adsorption is primarily physical in nature i.e. physisorption. This is in agreement with the value of the

standard free energy change (ΔG^o) of MB adsorption onto this active carbon (-5.78 to -6.28 kJ/mol.K) (Table 4). Typically, values of $\Delta G_{ads}^o \leq -20$ kJ/mol.K imply physisorption (i.e. electrostatic interaction between the charged adsorbate species and the adsorbent surface) while -20 kJ/mol. $< \Delta G_{ads}^o < -40$ kJ/mol.K values are associated with chemical adsorption (chemisorption)^{20,21}. Wu²⁴ reported this chemisorption range as $-80 \geq \Delta G_{ads}^o \leq -400$ kJ/mol.K. Based on the ΔG_{ads}^o values obtained, the mechanism of adsorption of MB on PFAC is, therefore, a physisorption mechanism, and the adsorption is spontaneous in nature as shown by the negative ΔG_{ads}^o values. The value of standard entropy of adsorption (ΔS_{ads}^o) for this process is negative (-19.20 J/mol.) (Table 4).

The results of negative ΔH , ΔG and ΔS were obtained for adsorption of MB molecules on PFAC. This could be explained from the point that adsorbed molecules have at the most, two degrees of transitional freedom on the adsorbent surface and as a result, the rotational freedom of adsorbed species must always be less than that of the gas-phase molecules²⁴. Inevitably, the entropy-change on adsorption, $\Delta S = S_{ads} - S_{gas}$, must be negative. This imply decreased randomness at the adsorbent-adsorbate interface, which corresponds to decreased degree of freedom in the system and indicates low affinity of the adsorbent for adsorbate molecules^{3,9}. For a meaningful adsorption to occur, the free energy change on adsorption (ΔG) must also be negative. Since $\Delta G = \Delta H - T\Delta S$, the condition of meaningful adsorption requires that ΔH be negative (i.e. exothermic adsorption). This is generally true for adsorption from liquid phase also, though exceptions are possible^{25,26}.

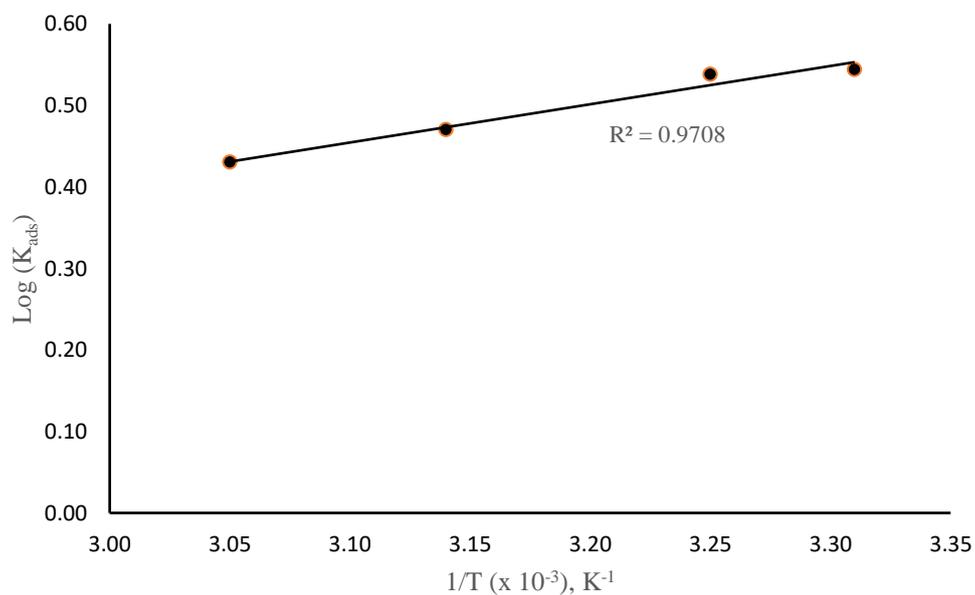


Figure 9: Vant-Hoff Plot for Adsorption of 2 mg MB Solution on PFAC at 302-328 K

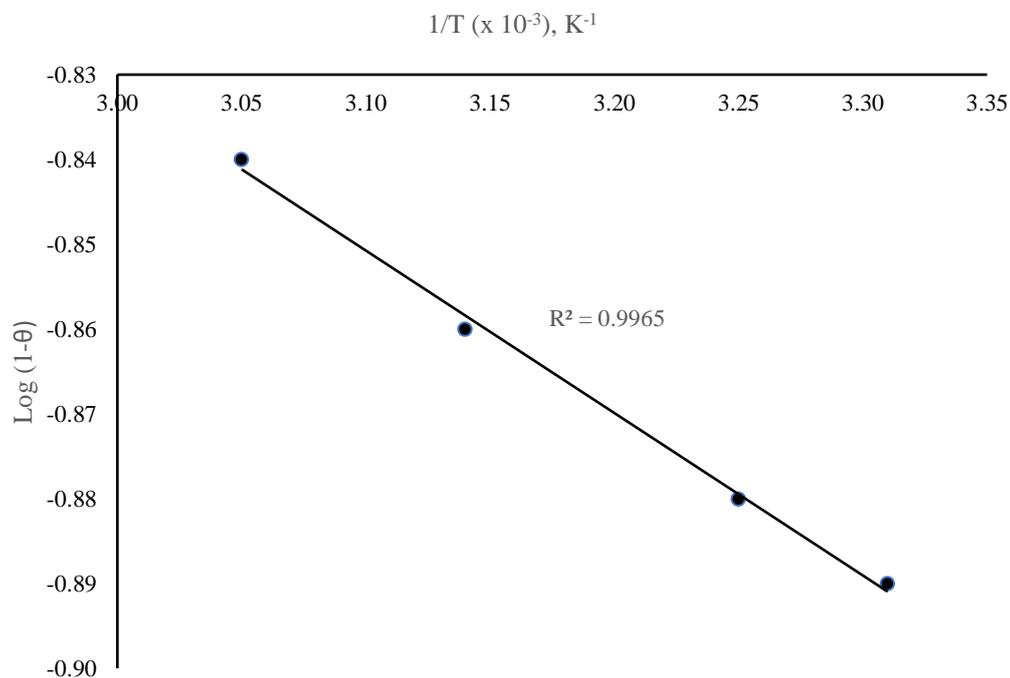


Figure 10: Plot of $\log(1 - \theta)$ for 2 mg MB Solution on PFAC Against Inverse of Temperature

Table 4: Thermodynamic and Related Parameters for MB Adsorption on Active PFAC Carbon

Parameters	Temperature (K)			
	302	308	318	328
Q_o (mg/g)	10.29	10.14	7.31	6.72
b (L/mg)	0.34	0.34	0.40	0.40
K_{ads} (L/mol.)	3.50	3.45	2.95	2.69
ΔG° (kJ/mol.K)	-5.78	-5.90	-6.09	-6.28
ΔH° (kJ/mol.)		-9.00		
ΔS° (J/mol.K)		-19.20		
E_a (kJ/mol.)		-3.60		
ξ°		0.55		

The negative value of the activation energy for adsorption of MB molecules on this active carbon (Table 4), indicates exothermic nature of the adsorption process and agrees with the earlier suggested exothermic nature based on decrease in adsorption capacity with increase in temperature, and the negative ΔH_{ads}° values. The sticking probability (ξ°) value (0.55) obtained for the adsorption of MB molecules on PFAC is less than unity. Sticking probability values in the range $0 < \xi^\circ < 1$, depending on temperature of the system, are desirable for processes²³. Therefore, the probability of the MB molecules to stick on the surface of this active carbon is high.

CONCLUSION

Polyfurfuryl alcohol carbon was investigated for adsorption (of MB molecules) from aqueous medium based on adsorption isotherms, kinetics and thermodynamics. The equilibrium data suggests that MB adsorption on PFAC is better modeled by the Langmuir isotherm. The adsorption on the carbon is feasible, spontaneous, exothermic, physical in nature

and follows the pseudo-second order kinetics.

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