

Isotherm and Thermodynamic Analysis on the Adsorption of Rhodamine B Dye onto *Borassus flabellifer* bark Nano Carbon

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Abstract: Application of activated *Borassus flabellifer* bark nano carbon (ABNC) for the removal of a Cationic dye, Rhodamine B, from aqueous solutions has been investigated. The experiments were carried out in batch mode. Effect of the parameters such as pH, initial dye concentration and temperature on the removal of the dye was studied. Equilibrium was achieved in 60 min. Maximum adsorption of dye was achieved at pH 6.6. Removal percentage was found to be dependent on the initial concentration of dye solution, and maximum removal was found to be 96% at 25 mg/L of Rhodamine B. The removal increases from 80% to 96% when the initial concentration of dye solution decreases from 125 mg/L to 25 mg/L. The equilibrium adsorption data were analyzed by Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The (Langmuir) adsorption capacity of the adsorbent is found to be 232.16 mg/g at 303 K. Kinetic modeling of the process of removal was carried out and the process of removal was found to follow a pseudo second order model. The thermodynamic parameters such as change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined and the negative values of ΔG^0 indicated that the process of removal was spontaneous at all values of temperatures. Further, the values of ΔH^0 indicated the endothermic nature of the process of removal.

Key words: Activated *Borassus flabellifer* bark nano carbon (ABNC); Rhodamine-B dye; Adsorption isotherm; Kinetics; Equilibrium models.

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I. Introduction

With the revolution in textile industries, they discharge colored effluents such as organic dyes like methylene blue and rhodamine-B to water bodies. These colored effluents have large amounts of suspended organic solids which are harmful to human beings and toxic for organisms. The removal of these dyes from wastewater has a considerable attention over the past decades to decrease their impact on the environment [1]. Several physical and chemical methods have been developed for the removal of organic dyes from industrial effluents [2]. Physical methods, mainly adsorption on various supports were recognized to be a promising and effective process to remove dyes from industrial waste water completely [3, 4]. The main advantages of adsorption are the reusability of material, low-cost, ease of operation and short time of operation. So it is necessary to develop effective adsorbents for the removal of dyes from textile effluents. Activated carbon is the most widely used adsorbent and can be prepared by physical activation in which carbonation or pyrolysis of the carbonaceous material at higher temperature (600-900°C) in an inert atmosphere followed by thermal activation at the same temperature in the presence of oxidizing agent such as air, steam and carbon dioxide or chemical activation in which pyrolysis and activation carried out only in one step simultaneously in presence of dehydrating agent such as H₃PO₄, HNO₃, KOH, NaOH, H₂O₂, H₂SO₄. Chemically activated carbon has higher yield, more surface area and better development of porous structure than that obtained by physical activation [5]. Several attempts have been made for the preparation of activated carbon from agriculture wastes.

In this article, we have reported the use of natural bio materials as an alternative due to their relative abundance and their low commercial values. *Borassus flabellifer* bark is the most ancient plant of India. It is found throughout India, especially in Tamil Nadu, Kerala and Bengal. The aerial parts of the tree have

medicinal values and this work aimed at the possibility of using wastes of a *Borassus flabellifer* bark as an adsorbent for the adsorption of cationic dye Rhodamine-B from aqueous solution.

II. Materials and Methods

All reagents used in the experiments were of analytical (AR) grade and were obtained from scientific equipment company Trichy. Stock solutions of the test reagents were prepared by dissolving the dye in distilled water.

2.1 Preparation of adsorbent

The natural plant material *Borassus flabellifer* bark used in the present investigations was collected from Muthupet nearby Thiruvavur district. The bark wastes were washed with distilled water several times to remove the dirt and dust and were subsequently dried in a hot air oven at 110°C. After that, carbonization of the *Borassus flabellifer* bark was carried out by w/v ratio of concentrated sulphuric acid for 24 hour; the primary carbon was activated at 1100°C for 6 hours under optimized conditions to obtain activated nano carbon. The activated nano carbon was thereafter transferred to room temperature in an inert atmosphere of nitrogen and washed with hot distilled water and 0.5 N hydrochloric and until the pH of the material reached 7.0. The activated nano carbon was also dried in a hot air oven at 110°C, ground and sieved to obtain the desired particular size (45nm) and stored in desiccators for further use.

2.2 Experimental Procedure

Batch experiments were conducted to study the influence of important parameters like the pH, contact time, initial dye concentration and temperature on the removal of Rh-B onto activated *Borassus flabellifer* bark nano carbon (ABNC). For Adsorption isotherms, dye solution of different concentrations (25-125 mg/L) and at different temperatures (30- 60 °C) with known pH and known amount of adsorbent (25mg/L) were agitated at 120rpm until the equilibrium was reached. Then the solution was kept to settle down and the residual concentration of Rh-B was analyzed by UV-Visible spectrophotometer at 554 nm. All experiments were carried out at normal pH for Rh-B. Effect of pH on dye removal was studied over a pH range of 2.0-9.0. The initial pH of the solution was adjusted by addition of acetate or phosphate buffers. The effect of sorbent dosage on adsorption rate was investigated using the procedures described above. The percentage of dye removal was calculated using the following equation.

$$q_{(t)} = \frac{((C_{(i)} - C_{(t)}) \times V)}{m} \quad (1)$$

Where, $q_{(t)}$ is the mass of adsorbed dye per unit mass of adsorbent (mg^{-1}) $C_{(i)}$ and $C_{(t)}$ are the initial and actual concentration (g dm^{-3}) of dye at time t , respectively. V is the volume of the treated solution (ml) and m is the mass of adsorbent (g) The adsorption degree, AD as a function of time was also determined from the experimental data using the following relationship

$$\text{AD}\% = \frac{(1 - C_{(t)}) \times 100}{C_i} \quad (2)$$

Based on the adsorption kinetics experiments, the process time for the equilibrium adsorption experiments was chosen, long enough assuming that the considered sorbent / sorbate system is equilibrated.

III. Result and Discussion

3.1 Effect of Contact time:

In order to establish the equilibration time for maximum uptake and to know the kinetics of the adsorption process, Rh-B adsorption on ABNC adsorbent was investigated as a function of contact time and the results were shown in fig 1. The figure shows that the uptake rate was initially rapid with 50% of the adsorption completed within 30min, Equilibrium was achieved within 45 min therefore, an equilibration period of 1hr was selected for all further experiments. The time profile of Rh-B uptake is a single smooth and continuous curve leading to saturation suggesting the possible monolayer coverage of Rh-B on the surface of the adsorbent.

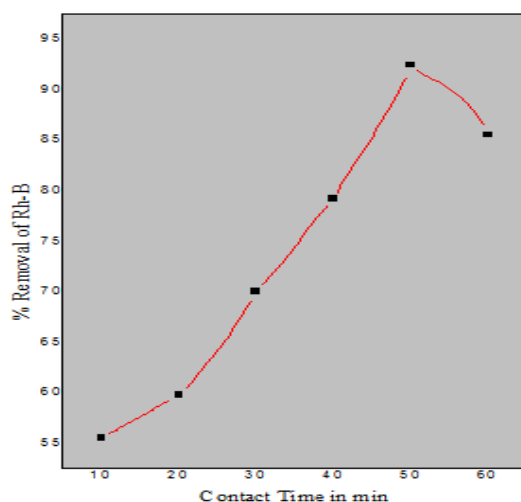


Fig. 1-Effect of contact time on the adsorption of Rh-B dye on ABNC

3.2 Effect of adsorbent dosage

The adsorption of the Rh-B dye on ABNC was studied by varying the adsorbent dose (25–125 mg/50ml) for 50 mg/L of dye concentration. The percentage of adsorption increased with increase in the ABNC dose, which is attributed to increased carbon surface area and the availability of more adsorption sites [6, 7]. Hence, all studies were carried out with 0.025g of adsorbent/50 ml of the varying adsorbate solutions. 25, 50, 75, 100 and 125 mg/L. The results obtained from this study are shown in figure 2. The amount of Rh-B adsorbed per gram is reduced with increase in the dosage of ABNC. This reveals that the direct and equilibrium capacities of Rh-B are functions of the activated ABNC dosage.

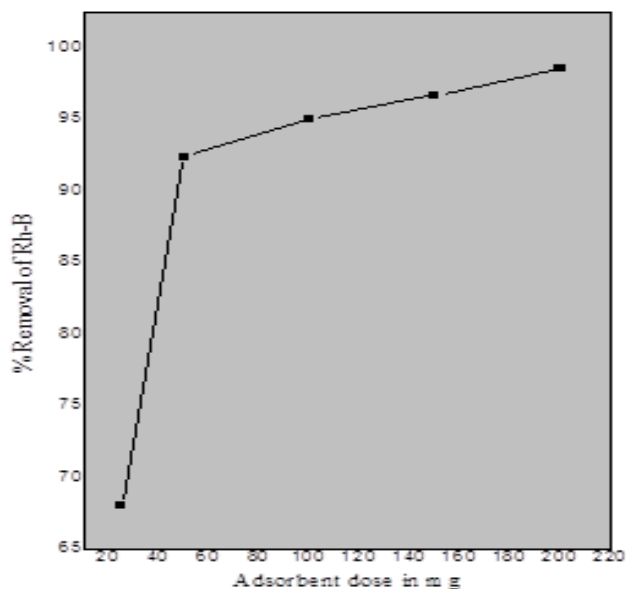
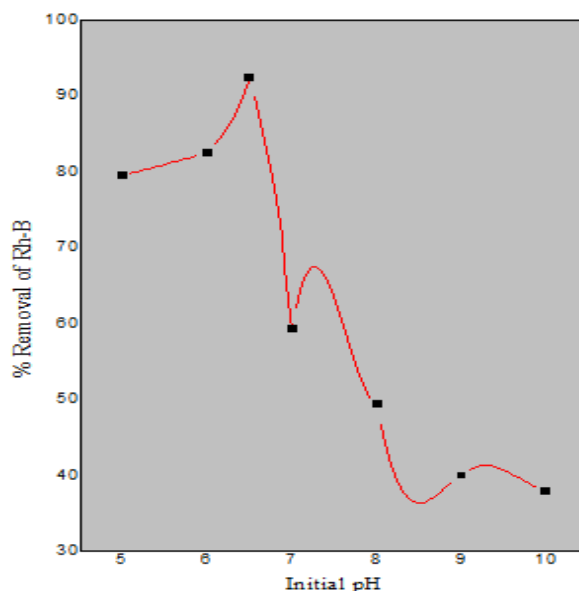


Fig.2-Effect of Adsorbent dose on the removal of Rh-B [RhB]=50mg/L;contact time =60 min;temperature 30 °C

3.3 Effect of Initial pH.

Previous research [8] has shown that the adsorption of dye molecules onto an adsorbent is highly pH dependent since, the functional groups, which are responsible for interaction between dye molecules and adsorbent, can be protonated or deprotonated to produce different surface charges in solution at different pH values. Therefore the effects of initial solution pH were studied in the pH range of 2-9 for Rh-B. The percentage removal increased from 76 % to 92 % upto pH7 whereas it decreased after pH 7 for Rh-B (Fig 3). The pH_{zpc} of any adsorbent is a very important characteristic that determines the pH at which the surface has net electrical neutrality. It is well-known that for basic dye adsorption, negatively charged groups on the adsorbent are

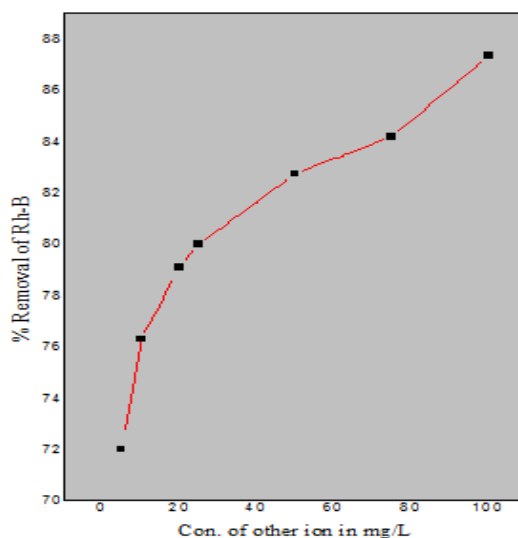
necessary. At lower pH values ($\text{pH} < \text{pH}_{\text{zpc}}$) the surface charge of the surface of ABNC may get positively charged as a result of being surrounded by H_3O^+ ions and thus the competitive effects of H_3O^+ ions as well as the electrostatic repulsion between the dye molecules and the positively charged active adsorption sites on the surface of the ABNC lead to a decrease in the uptake of dye molecules. In contrast at higher pH values ($\text{pH} > \text{pH}_{\text{zpc}}$) the surface of ABNC may acquire a negative charge leading to an increase in dye uptake due to the electrostatic force of attraction. On the other hand no valid reason can be given for the decrease in the adsorption amount of Rh-B after pH 7. Similar results were obtained for the adsorption of Rhodamine-B onto ABNC. As a result, the initial pH value was optimized as 6.6 for dye.



Fig,3-Effect of pH on the adsorption of Rh-B dye on ABNC

3.4 Effect of other ions:

The effect of other ion like Cl^- on the adsorption process studied at different concentrations. The ions added to 50mg/L of Rh-B solutions and the contents were agitated for 60 min at 30°C. The results shown in the Fig. 4 reveals that low concentration of Cl^- does not affect the percentage of adsorption of Rh-B on ABNC, because the interaction of Cl^- at available sites of adsorbent through competitive adsorption is so effective. While the concentration of other ion increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption is not so effective and due to the formation of electrical double layer, hence the percentage adsorption increases [9].



Fig,4 -Effect of other ion on the adsorption of Rh-B dye on ABNC

3.5 Adsorption Models

Adsorption isotherm [6-10] describes the relation between the amount or concentration of adsorbate that accumulates on the adsorbent and the equilibrium concentration of the dissolved adsorbate. Equilibrium studies were carried out by agitating a series of beakers containing 100 mL of rhodamine B dye solutions of initial concentration 25-125 mg/L with 0.025 g of ABNC at 30 °C with a constant agitation. Agitation was provided for 1.0 h, which is more than sufficient time to reach equilibrium.

Formula used for calculation of q_e is as follows:

$$q_e = \frac{C_0 - C_e}{m} \times V$$

3.5.1 Freundlich adsorption isotherm

The Freundlich adsorption isotherm is based on the equilibrium sorption on heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to heat of adsorption. The adsorption isotherm is expressed by the following equation

$$q_e = K_F C_e^{1/n_F} \quad \dots \dots \dots (3)$$

Which, can be linearized as

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad \dots \dots \dots (4)$$

Where, q_e is the amount of MG dye adsorbed at equilibrium (mg/g) and C_e is the concentration of MG dye in the aqueous phase at equilibrium (ppm). K_F (L/g) and $1/n_F$ are the Freundlich constants related to adsorption capacity and sorption intensity, respectively.

The Freundlich constants K_F and $1/n_F$ were calculated from the slope and intercept of the $\ln q_e$ Vs $\ln C_e$ plot. The model parameters are shown in Table 2. The magnitude of K_F showed that ABNC had a high capacity for Rh-B dye adsorption from the aqueous solutions studied. The Freundlich exponent, n_F , should have values in the range of 1 and 10 (i.e., $1/n_F < 1$) to be considered as favourable adsorption [23]. $1/n_F$ value of less than 1 indicated that RH-B dye is favorably adsorbed by ABNC. The Freundlich isotherm did not show a good fit to the experimental data as indicated by SSE and Chi-square statistics.

M_b	C_e (Mg/L)				Q_e (Mg/L)				Removal %			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
25	1.7163	1.0298	0.6873	0.6522	46.568	47.941	48.625	48.696	93.135	95.881	97.251	97.391
50	3.7758	3.4341	3.1037	2.4036	92.449	93.13	93.793	95.193	92.449	93.132	93.793	95.193
75	8.2663	7.4843	6.5218	6.0427	133.47	135.03	136.96	137.91	88.978	90.021	91.304	91.943
100	12.0426	11.0130	10.4465	9.7990	175.91	177.97	179.11	180.40	87.957	88.987	89.553	90.201
125	17.8490	17.2298	16.8496	15.8490	214.30	215.54	216.30	218.30	85.721	86.216	86.520	87.321

Table: 1. Equilibrium parameters for the adsorption of Rh-B dye

3.5.2 Langmuir adsorption isotherm

The Langmuir adsorption isotherm is based on the assumption that all sorption sites possess equal affinity to the adsorbate. The Langmuir isotherm in a linear form can be represented as: [23]

$$\dots \dots \dots (5) \quad \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Where q_e is the amount of Rh-B dye adsorbed at equilibrium (mg/g), C_e is the concentration of Rh-B in the aqueous phase at equilibrium (ppm), q_m is the maximum Rh-B dye uptake (mg/g), and K_L is the Langmuir constant related to adsorption capacity and the energy of adsorption (g/mg). A linear plot of C_e/q_e Vs C_e was employed to determine the value of q_m and K_L , the data so obtained are also presented in Table 2. The model predicted a maximum value that could not be reached in the experiments. The value of K_L decreased with an increase in the temperature. A high K_L value indicates a high adsorption affinity. Weber and Chakraborti [24] expressed the Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter (R_L) which is defined in the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \dots\dots\dots (6)$$

Where, C_0 is the initial Rh-B dye concentration (ppm). Four scenarios can be distinguished:

The sorption isotherm is unfavorable when $R_L > 1$, the isotherm is linear when $R_L = 1$, The isotherm is favorable when $0 < R_L < 1$ and the isotherm is irreversible when $R_L = 0$. The values of dimensionless separation factor (R_L) for Rh-B dye removal were calculated at different concentrations and temperatures. As shown in Table 3, at all concentrations and temperatures tested the values of R_L for Rh-B dye adsorptions on the ABNC were less than 1 and greater than zero, indicating favorable adsorption.

The Langmuir isotherm showed a better fit to the adsorption data than the Freundlich isotherm. The fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the ABNC surface, since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	$K_f(\text{mg/g}) (\text{L/mg})^{1/n}$	35.410	47.373	57.010	60.656
	n	1.5680	1.8630	2.1128	2.1308
Langmuir	$Q_m(\text{mg/g})$	338.37	288.75	268.28	264.14
	b (L/mg)	0.0910	0.1488	0.2051	0.2432
Temkin	$b_T (\text{J/mol})$	69.702	58.535	51.713	52.100
	$K_T (\text{L/mg})$	1.062	2.156	2.842	3.099
Hurkins-Jura	$A_H (\text{g}^2/\text{L})$	-2465.8	-2963.1	-3393.1	-3517.6
	$B_H (\text{mg}^2/\text{L})$	-1.1517	-1.1303	-1.1138	-1.0812
Halsay	$K_{Ha}(\text{mg/L})$	268.6	1323.0	5128.6	6293.6
	n_{Ha}	1.5680	1.8630	2.1128	2.1308
Radlich-Peterson	g	0.3622	0.4632	0.5267	0.5307
	$K_R (\text{L/g})$	0.0282	0.0211	0.0175	0.0165
Dubinin-Radushkevich	$q_s (\text{mg/g})$	169.32	159.81	157.16	161.67
	$K_D \times 10^{-4} \text{ mol}^2 \text{ kJ}^{-2}$	1.6372	1.6170	1.6077	1.6129
Jovanovic	$K_J (\text{L/g})$	0.0859	0.0859	0.0848	0.0882
	$q_{\text{max}} (\text{mg/g})$	55.142	59.275	63.080	65.168
BET	$C_{\text{BET}} (\text{L/mg})$	13.093	23.500	36.065	42.492
	$q_s (\text{mg/g})$	0.0764	0.0426	0.0277	0.0235

Table: 2. Isotherm parameters for the adsorption of Rh-B dye

3.5.3 Temkin adsorption isotherm:

The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent-adsorbate interactions [25]. The Temkin isotherm equation is given as:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \dots\dots\dots(7)$$

Which, can be represented in the following linear form

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \dots\dots\dots(8)$$

Where, $K_T (\text{L/g})$ is the Temkin isotherm constant, $b_T (\text{J/mol})$ is a constant related to heat of sorption, R is the ideal gas constant (8.314 J/mol K), and T is absolute temperature (K). A plot of q_e versus $\ln C_e$ enables the determination of isotherm constants K_T and b_T from the slope and intercept, The model parameters are listed in Table 2. The Temkin isotherm appears to provide a good fit to the Rh-B dye adsorption data.

The adsorption energy in the Temkin model, b_T , is positive for Rh-B dye adsorption from the aqueous solution, which indicates that the adsorption is endothermic. The experimental equilibrium curve is close to that predicted by Temkin model. Consequently, the adsorption isotherm of Rh-B dye on ABNC can be described reasonably well by the Temkin isotherm.

3.5.4 Hurkins-Jura adsorption isotherm

The Hurkins-Jura adsorption isotherm can be expressed as ^{[26]:}

$$q_e = \sqrt{\frac{A_H}{B_H + \log C_e}} \dots\dots\dots(9)$$

This can be rearranged as follows:

$$\frac{1}{q_e^2} = \frac{B_H}{A_H} - \frac{1}{A_H} \log C_e \dots\dots\dots(10)$$

Where, A_H (g^2/L) and B_H (mg^2/L) are two parameters characterizing the sorption equilibrium.

The isotherm equation accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution. The Harkins–Jura isotherm parameters are obtained from the plots of $1/q_e^2$ versus $\log C_e$ enables the determination of model parameters A_H and B_H from the slope and intercept in table 2.

3.5.5 Halsey adsorption isotherm

The Halsey adsorption isotherm can be given as [27]:

$$q_e = \exp\left(\frac{\ln K_{Ha} - \ln C_e}{n_{Ha}}\right) \dots\dots\dots(11)$$

And, a linear form of the isotherm can be expressed as follows:

$$\ln q_e = \frac{\ln K_{Ha}}{n_{Ha}} - \frac{\ln C_e}{n_{Ha}} \dots\dots\dots(12)$$

Where, K_{Ha} (mg/L) and n_{Ha} are the Halsey isotherm constants.

A plot of $\ln q_e$ Vs $\ln C_e$, enables the determination of n_{Ha} and K_{Ha} from the slope and intercept. This equation is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of adsorbent. The result shows that the experimental data and the model predictions are based on the non-linear form of the Halsey models. The model parameters are listed in Table 2. This result also shows that the adsorption of Rh-B dye on ABNC was not based on significant multilayer adsorption. The Halsey model is also not suitable to describe the adsorption of Rh-B dye on ABNC, because this model also assumes a multilayer behavior of the adsorption of adsorbate onto adsorbent.

3.5.6 Radish-Peterson adsorption isotherm

The Radlich-Peterson adsorption isotherm contains three parameters and incorporates the features of Langmuir and Freundlich isotherms into a single equation. The general isotherm equation can be described as follows [28]:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \dots\dots\dots(13)$$

The linear form of the isotherm can be expressed as follows:

$$\ln \frac{C_e}{q_e} = g \ln C_e - \ln K_R \dots\dots\dots(14)$$

Where, K_R (L/g) and a_R (L/mg) are the Radlich-Peterson isotherm constants and g is the exponent between 0 and 1. There are two limiting cases: Langmuir form for $g = 1$ and Henry's law for $g = 0$. A plot of $\ln C_e/q_e$ versus $\ln C_e$ enables the determination of isotherm constants g and K_R from the slope and intercept. The values of K_R , presented in Table 2, indicate that the adsorption capacity of the ABNC decreased with an increase temperature. Furthermore, the value of g lies between 0 and 1, indicating favorable adsorption.

(C _i)	Temperature °C			
	30°C	40°C	50°C	60°C
25	0.3053	0.2119	0.1632	0.1412
50	0.1802	0.1185	0.0889	0.0760
75	0.1278	0.0823	0.0611	0.0520
100	0.0990	0.0630	0.0465	0.0395
125	0.0808	0.0510	0.0375	0.0318

Table: 3. Dimensionless separation factor (r_1) for the adsorption of Rh-B dye

3.5.7 Dubinin-Radushkevich adsorption isotherm

The Dubinin-Radushkevich adsorption isotherm is another isotherm equation [32]. It is assumed that the characteristic of the sorption curve is related to the porosity of the adsorbent. The linear form of the isotherm can be expressed as follows [29]:

$$\ln q_e = \ln Q_D - B_D \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \dots\dots\dots(15)$$

Where, Q_D is the maximum sorption capacity (mol/g), and B_D is the Dubinin-Radushkevich constant (mol^2/kJ^2). A plot of $\ln q_e$ Vs $R_T \ln (1+1/C_e)$ enables the determination of isotherm constants B_D and Q_D from the slope and intercept.

3.5.8 Jovanovich adsorption isotherm

The model of an adsorption surface considered by Jovanovic [30] is essentially the same as that considered by Langmuir. The Jovanovic model leads to the following relationship [29]:

$$q_e = q_{\max} \left(1 - e^{-K_J C_e} \right)$$

The linear form of the isotherm can be expressed as follows:

$$\ln q_e = \ln q_{\max} - K_J C_e$$

Where, K_J (L/g) is a parameter. q_{\max} (mg/g) is the maximum Rh-B dye uptake. The q_{\max} is obtained from a plot of $\ln q_e$ and C_e . Their related parameters are listed in Table 2.

By comparing the values of the error functions, it was found the Langmuir and Temkin models are best to fit the Rh-B adsorption on the ABNC. Both models show a high degree of correlation. This is clearly confirming the good fit of Langmuir and Temkin models with the experimental data for removal of Rh-B dye from the solution.

3.5.9 The Brunauer–Emmett–Teller (BET) isotherm model

Brunauer–Emmett–Teller (BET) ^[31] isotherm is a theoretical equation, most widely applied in the gas–solid equilibrium systems. It was developed to derive multilayer adsorption systems with relative pressure ranges from 0.05Pa to 0.30Pa corresponding to a monolayer coverage lying between 0.50Pa and 1.50Pa. Its extinction model related to liquid–solid interface is exhibited as:

$$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)(C_e / C_s)]} \dots\dots\dots(16)$$

Where, C_{BET} , C_s , q_s and q_e are the BET adsorption isotherm (L/mg), adsorbate monolayer saturation concentration (mg/L), theoretical isotherm saturation capacity (mg/g) and equilibrium adsorption capacity (mg/g), respectively. As C_{BET} and $C_{BET} (C_e / C_s)$ is much greater than 1, the linear form is represented as

$$\frac{C_e}{q(C_s - C_e)} = \frac{1}{q_s C_{BET}} + \left(\frac{C_{BET} - 1}{q_s C_{BET}} \right) \left(\frac{C_e}{C_s} \right) \dots\dots\dots(17)$$

Where, C_e is equilibrium Concentration (mg/l), C_s is adsorbate monolayer saturation concentration (mg/l) and C_{BET} is BET adsorption relating to the energy of surface interaction (l/mg). The results of BET model are also shown in table 2. The results predict the physisorption mechanism and monolayer coverage of adsorbate on ABNC

3.6 Kinetic parameters

The rate and mechanism of the adsorption process can be elucidated based on kinetic studies. Dye adsorption on solid surface may be explained by two distinct mechanisms: (1) An initial rapid binding of dye molecules on the adsorbent surface; (2) relatively slow intra-particle diffusion. To analyze the adsorption kinetics of the dye, the pseudo-first-order, the pseudo-second-order, and intra-particle diffusion models were applied [38, 39]. Each of these models and their linear modes of the equations are presented in below.

Kinetic Models and Their Linear Forms		
Model	Nonlinear Form	Linear Form
Pseudo-first-order	$dq_t/dt = k_1(q_e - q_t)$	$\ln (q_e - q_t) = \ln q_e - k_1 t \dots\dots\dots (18)$
Pseudo-second-order	$dq_t/dt = k_2(q_e - q_t)^2$	$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \dots\dots\dots (19)$

Where, q_e and q_t refer to the amount of (Rh-B) dye adsorbed (mg/g) at equilibrium and at any time, t (min), respectively and k_1 (1/min), k_2 (g/mg. min) are the equilibrium rate constants of pseudo-first order and pseudo-second order models, respectively.

Pseudo-first order model is a simple kinetic model, which was proposed by Lagergren [40] during 1898 and is used for the estimation of the surface adsorption reaction rate. The values of $\ln (q_e - q_t)$ were linearly correlated with t . The plot of $\ln (q_e - q_t)$ vs. t should give a linear relationship from which the values of k_1 will be determined from the slope of the plot. In many cases, the first-order equation of Lagergren does not fit well with the entire range of contact time and is generally applicable over the initial stage of the adsorption processes ⁽⁴¹⁾.

In the pseudo-second order model ⁽⁴²⁾, the slope and intercept of the t/q_t vs t plot were used to calculate the second-order rate constant, k_2 . The values of equilibrium rate constant (k_2) are presented in Table 4. According to Table 4, the value of r^2 (0.999) related to the pseudo-second order model revealed that Rh-B dye adsorption followed this model, which is in agreement with the results obtained by Karagozet *al.*[23], Hameed

et al.[24], and Altenoret *al.* [37]. Nevertheless, pseudo-first order and pseudo-second order kinetic models cannot identify the mechanism of diffusion of dye into the adsorbent pores.

C ₀	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q _e	k ₂	γ	h	α	β	γ	K _{id}	γ	C
25	30	49.39	0.0045	0.9866	11.06	11.900	0.2092	0.9894	0.1116	0.9961	1.7652
	40	49.47	0.0085	0.9858	20.74	76.205	0.3486	0.9914	0.0627	0.9888	1.8669
	50	49.60	0.0134	0.9886	32.85	30.073	0.5223	0.9954	0.0406	0.9907	1.9135
	60	49.62	0.0141	0.9897	34.81	116.27	0.5504	0.9924	0.0384	0.9897	1.9182
50	30	96.20	0.0032	0.9919	29.38	66.621	0.1459	0.9958	0.0789	0.9944	1.8189
	40	96.68	0.0035	0.9886	32.30	137.12	0.1527	0.9904	0.0745	0.9897	1.8312
	50	97.28	0.0039	0.9912	36.51	314.23	0.1602	0.9924	0.0700	0.9887	1.8447
	60	98.12	0.0042	0.9929	40.56	162.29	0.1768	0.9894	0.0624	0.9907	1.8635
75	30	137.05	0.0032	0.9869	59.71	23.547	0.1454	0.9904	0.0538	0.9947	1.8476
	40	139.39	0.0035	0.9860	67.39	85.275	0.1338	0.9965	0.0575	0.9887	1.8516
	50	141.97	0.0030	0.9852	60.38	96.079	0.1148	0.9951	0.0665	0.9907	1.8420
	60	141.77	0.0042	0.9854	83.67	165.31	0.1352	0.9967	0.0557	0.9887	1.8663
100	30	181.30	0.0031	0.9873	103.50	71.012	0.0992	0.9941	0.0596	0.9928	1.8413
	40	183.33	0.0030	0.9882	99.21	60.185	0.0973	0.9899	0.0602	0.9897	1.8441
	50	184.29	0.0031	0.9903	106.23	103.34	0.0997	0.9930	0.0583	0.9952	1.8507
	60	185.63	0.0031	0.9914	107.43	118.95	0.0998	0.9961	0.0578	0.9908	1.8547
125	30	220.04	0.0019	0.9901	91.24	11.336	0.0847	0.9908	0.0578	0.9910	1.8237
	40	221.45	0.0019	0.9922	90.78	97.180	0.0834	0.9967	0.0584	0.9897	1.8252
	50	221.83	0.0020	0.9869	96.59	280.68	0.0883	0.9954	0.0548	0.9907	1.8333
	60	224.13	0.0018	0.994	91.12	100.65	0.0825	0.9924	0.0583	0.9939	1.8304

Table: 4 the kinetic parameters for the adsorption of Rh-B dye onto ABNC

3.6.1 The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t/dt = \alpha \exp(-\beta q_t) \dots\dots(20)$$

Where; α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation, Chien and Clayton [18] assumed $\alpha\beta t \gg 1$ and by applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq. (13) becomes:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \dots\dots\dots(21)$$

The Rh-B adsorption fits with the Elovich model, a plot of q_t vs $\ln(t)$ yields a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ln(\alpha\beta)$. The Elovich model parameters α , β , and correlation coefficient (γ) are summarized in table 4. The experimental data such as the initial adsorption rate (α) adsorption constant (β) and the correlation co-efficient (γ) calculated from this model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second-order kinetics models. This may be due to increase the pore or active site on the ABNC adsorbent.

3.6.2 Weber and Morris intra-particle diffusion model:-

Kinetic data was further analyzed using the Intra particle diffusion model based on the theory proposed by Weber and Morris [19]. The amount of Rh-B adsorbed (q_t) at time 't' was plotted against the square root of time ($t^{1/2}$), according to eq.

$$Q_t = k_{id} t^{1/2} + C \dots\dots\dots(22)$$

Where, k_{id} is the Intraparticle diffusion rate constant and c is the intercept related to the thickness of the boundary layer. According to above equation a plot of q_t versus $t^{1/2}$ gives a straight line from the origin which says that the adsorption mechanism follows the intra-particle diffusion process only. However, the data exhibit multi linear plots, says the process are governed by two or more steps, It is clear from that, there are two separate zones: first linear portion (phase I) and second linear part (phase II). The first linear portion (Phase I) can be attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surface, phase II may be attributed to very slow diffusion of the adsorbate from the surface site in to the inner pores. Thus initial portion of Rh-B adsorption by adsorbent may be governed by the initial intra particle transport of Rh-B controlled by surface diffusion process and the later part controlled by pore diffusion. However, the intercept of the line fails to pass through the origin which may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of the straight lines from the origin reveals that the pore diffusion is not the sole rate - controlling.

3.7 Thermodynamic parameters

Thermodynamic parameters [15] were evaluated to confirm the adsorption nature of the present study. The thermodynamic constants, free energy change, enthalpy change and entropy change were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. Enthalpy change (ΔH), and entropy change (ΔS) may be determined from Van't Hoff equation:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (23)$$

By plotting ln K as ordinate and 1/T as abscissa, ΔS and ΔH were obtained by using the following equation the value of ΔG were obtained.

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots (24)$$

Where, ΔG is the free energy change (kJ mol⁻¹), R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), K the thermodynamic equilibrium constant and T is the absolute temperature (K).

$$\Delta G = \Delta H - T\Delta S = -RT \ln K_c \dots\dots\dots (25)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (26)$$

$$2.30 \log \frac{q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (27)$$

$$\log \frac{q_e}{C_e} = \frac{\Delta S}{R \times 2.303} - \frac{\Delta H}{RT \times 2.303} \dots\dots\dots (28)$$

The values of ΔS, ΔH, ΔG was obtained from a plot of log (q_e/C_e) vs. 1/T.

Heat of reaction (ΔH) for physical adsorption is reported to be 4.2 to 63 kJ/ mol in literature. The value of ΔH range from -8.89 to -11.543 kJ/mol from Table-5, which indicates that the nature of adsorption of Rhodamine B dye onto ABNC is a physical adsorption one. The positive value of ΔH & negative ΔG indicate endothermic and spontaneous process of adsorption of Rhodamine B (Rh-B) dye on ABNC respectively.

(C ₀)	ΔG°				ΔH°	ΔS°	E _a	S*
	30°C	40°C	50°C	60°C				
25	-6568.9	-8190.7	-9576.1	-10021.6	29.221	118.90	27963.2	9E-07
50	-6310.2	-6784.5	-7291.9	-8266.4	12.915	63.137	12123.4	6E-04
75	-5261.3	-5723.9	-6314.4	-6740.5	9.9922	50.321	9046.67	3E-03
100	-5009.1	-5437.2	-5769.8	-6145.6	6.3309	37.489	5641.86	1E-02
125	-4515.0	-4770.9	-4992.7	-5342.3	3.6555	26.920	3162.62	4E-02

Table: 5. Thermodynamic parameter for the adsorption of Rh-B dye onto ABNC

In order to support that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S*) were calculated from the experimental data. They were calculated by using the modified Arrhenius type equation related to surface coverage (θ) as follows⁴⁹:

$$\theta = \left(1 - \frac{C_e}{C_i} \right) \dots\dots\dots (29)$$

$$S^* = (1 - \theta)_e \frac{-E_a}{RT} \dots\dots\dots (30)$$

The sticking probability, S*, is a function of the adsorbate/adsorbent system under consideration but must satisfy the condition 0 < S* < 1 and is dependent on the temperature of the system. The values of E_a and S* were calculated from slope and intercept of the plot of ln(1-θ) versus 1/T respectively and are listed in Table 5.

From Table 5 it is clear that the reaction is spontaneous in nature as ΔG⁰ values are negative at all experimental temperatures. Again positive ΔH⁰ value confirms that the sorption is endothermic in nature. The positive value of ΔS⁰ reflects the affinities of the adsorbents for the Rh-B dye. The results shown in Table 5 indicate that the probability of the Rh-B dye to stick on surface of biomass is very high as S* << 1, these values confirm that, the sorption process is physisorption.

IV. Desorption studies

In order to assess the reusability of Rh-B-loaded ABNC biomass desorption experiments were carried out. The effect of strength of desorbing solution (HCl) on the recovery of Rh-B was analyzed. It is evident from the above result that when the strength of the desorbing solution increased from 0.5 to 2.0 M, Rh-B desorption percentage increased from 45 to 90%. Thus a significant amount of Rhodamine B is being desorbed, which shows that the ABNC biomass can be effectively reused after desorption [20].

V. Conclusions

On the basis of the above studies, the following can be concluded:

- I. Characterization of activated *Borassus flabellifer* bark nano carbon (ABNC) was carried out which revealed that the surface of the adsorbent was rough and suitable for adsorption.
- II. ABNC has shown a potential to remove Rhodamine B from aqueous solution.
- III. Initial concentration of the dye plays an important role in the removal process.
- IV. Kinetics of the process removal was studied and the values of rate constants were determined. The dye removal was found to be governed by film diffusion mechanism where external transport of the adsorbate over the surface of the adsorbent is greater than internal transport which was confirmed by the Ho plot and the process of removal was found to follow second order kinetics.
- V. Thermodynamic parameters were calculated for the removal of dye and their values indicated that the process of removal was spontaneous and endothermic.
- VI. The data were found to best fit in all isotherm models. It can therefore be concluded that activated *Borassus flabellifer* bark nano carbon (ABNC) offers promise as an economically viable alternative for sequestering the dye from the aqueous solution. The work can be extended for the removal of dyes from effluents as well.

Reference

- [1] Al Duri, B.; McKay, G.; El Geundi, M. S.; Wahab Abdul, M. Z. "Three Resistance Transport Model for dye Adsorption onto Bagasse Pitch". J. Environ. Eng. Div. ASCE, 1990, 116, 487.
- [2] S Arivoli, M Hema, S Parthasarathy and N Manju., Adsorption dynamics of methylene blue by acid activated carbon. J. Chem. Pharm. Res, 2010, 2(5), 626-641.
- [3] M Hema and S Arivoli, Rhodamine B adsorption by activated carbon: Kinetic and equilibrium studies, Indian Journal of Chemical Technology, 2009, 16(1), 38-45.
- [4] V Vijayakumaran, S Arivoli, and S Ramuthai, Adsorption of nickel ion by low cost carbon-kinetic, thermodynamic and equilibrium studies, 2009, 6 (S1), S347-S357.
- [5] Allen, S. J.; McKay, G.; Khader, K. Y. H. "Intraparticle Diffusions of Basic Dye During Adsorption onto Sphagnum Peat". Environ. Pollut. 1989, 56, 39.
- [6] Alpert, N. L.; Kesi, W. E.; Szymanaki, H. A. "Theory and Practice of Infrared Spectroscopy", 2nd ed.; Plenum: New York, 1970.
- [7] Crank, J. "The Mathematics of Diffusion" Clarendon Press: Oxford, 1956.
- [8] El-Geundi, M. S. "Colour Removal from Textile Effluents by Adsorption Technique" Wat. Res., 1991, 25, 271.
- [9] Fornwalt, H. J.; Hutchins, R. A. "Purifying Liquids with Activated Carbon". Chem. Eng. J, 1966, 73, 179.
- [10] Freundlich H, "The dye adsorption is losungen (Adsorption in Solution)", Z Phys, Chem. 1906, 57: 385 – 470.
- [11] Langmuir I, "The adsorption of gases plane surfaces of glass, mica and platinum". J. Am.Soc., 1918, 579, 1361 – 1403.
- [12] Freidal, R. A.; Queiser, J. A. "Infrared Analysis of Bitumenous Coal and Other Carbonaceous Materials". Anal. Chem, 1956, 28, 22.
- [13] Gadsen, J. A. "Infrared Spectra of Minerals and Related Inorganic Compounds" Butter worths: London, 1975.
- [14] Gupta, G. S.; Prasad, G.; Singh, V. N. "Removal of Chrome Dye from Carpet Effluents using Coal II (Rate process)". Environ. Technol. Lett., 1988, 9, 1413.
- [15] Namasivayam C, Munisamy N, Gayathri K, Rani M and Renganathan K, Biores Technol, 1995, 57, 37.
- [16] Weber T W, Chakravorti R K, "Pore and Solid diffusion models for fixed bed adsorbers". J. Am. Inst. Chem. Eng, 1974, 20, 228.
- [17] McKay G, Blair H S, Gardner J R, "Adsorption of dyes on chitin. I. Equilibrium Studies" J. Appl. Polym. Sci. 1982, 27, 3043 – 3057.
- [18] Chien S H, Clayton W R, "Application of Elovich Equation to the kinetics of Phosphate release and sorption on soil", Soil Sci. Soc. Am. J. 1980, 44, 265 – 268.
- [19] Weber W J, Morris J C, "Kinetics of adsorption on Carbon from solution". J. Sanitary Eng. Div. 1964, 90, 79.
- [20] Arivoli S Venkataraman B R, Rajachandrasekar T and Hema M, Res. J. Chem Environ., 2008, 17, 70-78.

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