

# THERMODYNAMIC AND KINETIC ANALYSIS ON THE REMOVAL OF RHODAMINE B DYE USING ACTIVATED NANO CARBON

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**Abstract:** In this work, batch adsorption experiments were carried out for the removal of Rhodamine B as a cationic dye from aqueous solutions using activated Carica papaya leaves carbon. The effects of major variables governing the efficiency of the process such as, temperature, initial dye concentration, adsorbent dosage, and pH were investigated. Experimental results have shown that, the amount of dye adsorption increased with increasing the initial concentration of the dye, adsorbent dosage, and temperature. Equilibrium data were fitted to the Langmuir, Freundlich, Temkin, Dubinin-Raduskevich, Harkins-Jura, BET isotherm models and isotherm constants were determined. The adsorption kinetic data were analyzed using pseudo-second-order and Elovich models. Thermodynamic parameters such as changes in the free energy of adsorption ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were calculated. The negative values of  $\Delta G^\circ$  indicate that the methylene blue adsorption process is spontaneous in nature and the positive value of  $\Delta H^\circ$  shows the endothermic nature of the process.

**Keywords:** Adsorption Activated Carbon, Kinetics, Thermodynamics, Isotherms.

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## 1. INTRODUCTION

Nowadays as a result of growing environmental awareness, the use of natural dye stuff obtained from vegetable and other animal sources have decreased substantially. They are replaced by synthetic dye stuffs produced on an industrial scale with its largest consumer being the textile industries [1]. More than 10,000 different types of dyes and pigments, with an annual production of more than 0.7 million tons are commercially available [2]. Unfortunately, during the dyeing process, a large percentage of the synthetic dye does not bind and is lost to the waste stream as residual dyes, approximately 5-10% dyes are released into the environment making the effluent highly coloured with breakdown products that are toxic, carcinogenic or mutagenic. Thus clearly, dyes are a potential hazard to living organisms [3]. Conventional waste water treatment methods for removing dyes include physicochemical, chemical and biological methods, but are very expensive and advance in technology [4]. Adsorption onto activated carbon process is one of the effective techniques that have been successfully employed for dyes removal from waste water because of its capability for adsorbing a broad range of different types of adsorbate efficiently, and its simplicity of design [4]. However, commercially available activated carbon is still considered expensive [5]. Groundnut shells are sometimes used for stock feed, but not as popular as cereal straws and legume stovers. Therefore, they can be used for the commercial production of activated carbon without much competition from livestock industry. Moreover, large quantities of groundnut shells can be obtained very cheaply from companies that are involved in shelling groundnut.

## 2. MATERIALS AND METHODS

### Preparation of the adsorbent:

The dried Carica papaya leaves were carbonized with concentrated sulphuric acid in the weight ratio of 1:1 (w/v). Heating for six hours in a furnace at 400°C has completed the carbonization and activation. The resulting carbon was washed with distilled water until a constant pH of the slurry was reached. Then the carbon was dried for four hours at 120°C in a hot air oven. The dried material was ground well to a fine powder and sieved.

### Preparation of the Adsorbate:

The stock solution was prepared by dissolving 1 g of Rhodamine B in 1000 ml of double distilled water. The test solutions were prepared by diluting stock solution to the desired concentrations. The concentration of the Rhodamine B dye was determined at 554 nm. The pH measurements were done using Digital pH meter (Equip-Tronics EQ 614A, India) and adsorption studies were carried out on UV-Vis Double Beam spectrophotometer (Systronics 2203, India). The Rhodamine B dye structure is given below.

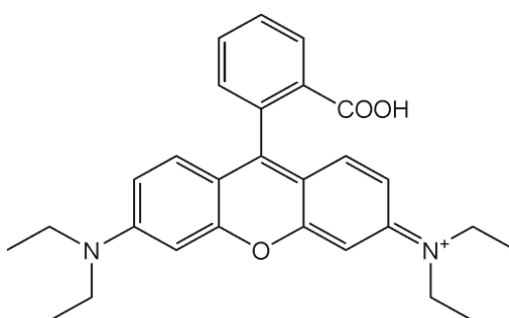


Fig.1: Structure of Rhodamine B

### Batch adsorption experiments:

The Batch adsorption experiments were conducted in 250 mL Erlenmeyer flask with 50mL of standard Rhodamine B solution and were agitated in a thermo state – controlled shaker at 120 rpm. All experiment were conducted at 30-60 °C, unless otherwise was stated.

The effect of initial pH on the adsorption of the Rhodamine B onto the activated carbon was studied across a pH range of 2.0 – 9.0 with a fixed adsorbent concentration (25 mg/50ml of 20mgL<sup>-1</sup> of Rhodamine B solution). The pit value of the initial metal solution (50mgL<sup>-1</sup>) was adjusted using a 0.1M HCl or NaOH solution. Activated nano carbon (0.0250g) was then added to the solution and agitated for enough time to achieve equilibrium. The effect of the agitation period was also studied at a constant concentration of 20 mg L<sup>-1</sup> Rhodamine B solution and a fixed adsorbent concentration of 25mg/50mL at the optimum pH. After agitation the sample solution was withdrawn at different time intervals (15-60min) and centrifuged at 1000 rpm for 10 min. Subsequently an aliquot of the supernatant was used for determination of the remaining Rhodamine B concentration, and the remainder was poured back into the original solution. The determination of the effect of the initial concentration of the uptake of the Rhodamine B was conducted by varying the Rhodamine B concentration from 10 to 50 mg L<sup>-1</sup> at a constant activated carbon dosage of 25 mg at optimum pH and agitation period. The effect of temperature on the adsorption characteristics was studied by determining the adsorption isotherms from 303 – 333K at a Rhodamine B concentration of 10-50mg/L.

The percentage removal of the Rhodamine B and the amount of Rhodamine B taken up by the adsorbent was calculated by applying following equations.

$$\% \text{ Removal} = \frac{C_i - C_t}{C_i} \times 100 \dots\dots\dots(1)$$

$$Q = \frac{(C_i - C_t)}{m} V \dots\dots\dots(2)$$

Where  $C_i$  and  $C_t$  are the initial and liquid phase concentrations of Rhodamine B at time 't' ( $\text{mg L}^{-1}$ )  $Q$  is the amount of Rhodamine B adsorbed on the adsorbent at any time ( $\text{mg g}^{-1}$ ),  $m$ (g) the mass of the adsorbent sample used and  $V$  the volume of the Rhodamine B solution (L).

### 3. RESULTS AND DISCUSSION

#### **Effect of contact time:**

In batch adsorption process contact time is one of the potent factors. In the resultant process all of the parameters except contact time, Temperature (30, 40, 50 and  $60^\circ\text{C}$ ), adsorbent dose (25 mg 125 mg to 50 ml) and agitation speed (120 rpm), were kept constant. The maximum removal of Rhodamine B by Activated Carica papaya leaves Nano Carbon required contact time of 60 minutes, this is represented (Figure 1), It was revealed that the removal of Rhodamine B increase with increase in contact time, and the optimal removal efficiency was reached within 50 minutes. There is the maximum adsorption occurs at 50 minutes after which the adsorption phase reaches an equilibrium. At this point maximum amount of Rhodamine B adsorbed under the particular conditions. (Figure 1), indicates that, the time variation curve is single, smooth and continuous and it shows the formation of monolayer coverage on the outer interface of the adsorbent.

#### **Effect of adsorbent dose:**

The adsorption of Rhodamine B by the adsorbent Carica papaya leaves was investigated using the following adsorbent doses: 0.025 to 0.125 g in 50 mL of 50 mg/L Rhodamine B by keeping other variables constant (at optimal pH of 6.5, shaker speed = 200 rpm, contact time = 40 min and temperature =  $30^\circ\text{C}$ ). After adsorption time was completed the adsorbents were removed from the solution and the concentration of residual dye in each solution was determined using ACPLNC.

#### **Effect of initial concentration:**

The experimental results of adsorptions of at various concentrations (10, 20, 30, 40 and 50 mg/L) percent adsorption decreased with increase in initial metal concentration, but the actual amount of Rhodamine B adsorbed per unit mass of carbon increased with increase in metal concentration. It means that the adsorption is highly dependent on initial concentration of metal. It is because of that at lower concentration, the ratio of the initial number of metals to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentrations.

#### **Effect of pH:**

The solution pH is one of the most important factors that control the adsorption of Rhodamine B on the adsorbent material. The adsorption capacity can be attributed to the chemical form of heavy metals in the solution at specific pH (i.e. Pure ionic metal form or metal hydroxyl form). In addition, due to different functional groups on the adsorbent surface, which become active sites for the metal binding at a specific pH the effect of adsorption can vary substantially. Therefore, an increase in pH may cause an increase or decrease in the adsorption, resulting different optimum pH values dependent on the type of adsorbent. To examine the effect of pH on the % removal of Rhodamine B, the solution pH were varied from 2.0 to 10.0 by adding acid and base to the stock solution This increases may be due to the presence of negative charge on the surface of the adsorbent that may be responds for the metal binding. However, as the pH is lowered, the hydrogen ions compete with metal ions for the adsorption sites in the adsorbent, the overall surface charge on the particles become positive and hinds the binding of positively charged metal ions. On other hand, decrease in the adsorption under  $\text{pH} > 6.5$  may be due to occupation of the adsorption sites by  $\text{OH}^-$  ions which retard the approach of such ions further toward the adsorbent surface. From the experimental results, the optimum pH range for the adsorption of the Rhodamine B ions is 2.0 to 6.5 shown in Figure.3.

#### **Adsorption Isotherm:**

##### **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

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

Which, can be linearized as

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

Where,  $q_e$  is the amount of Rhodamine B adsorbed at equilibrium (mg/g) and  $C_e$  is the concentration of Rhodamine B 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, as shown in Fig. 5, and the model parameters are shown in Table 2. The magnitude of  $K_F$  showed that ACPLNC had a high capacity for Rhodamine 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. A  $1/n_F$  value of less than 1 indicated that Rhodamine B dye is favorably adsorbed by ACPLNC. The Freundlich isotherm did not show a good fit to the experimental data as indicated by SSE and Chi-square statistics.

#### 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.

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

Where  $q_e$  is the amount of Rhodamine B dye adsorbed at equilibrium (mg/g),  $C_e$  is the concentration of Rhodamine B in the aqueous phase at equilibrium (ppm),  $q_m$  is the maximum Rhodamine 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  $K_L$ , as shown in Fig. 6, and the data so obtained were 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 expressed the Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter ( $R_L$ ) defined in the following equation:

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

Where,  $C_0$  is the initial Rhodamine 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 Rhodamine 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 Rhodamine B dye adsorptions on the ACPLNC 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 as shown in Fig. 5 and Fig. 6. The fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the ACPLNC surface, since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.

#### Temkin adsorption isotherm:

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

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

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,  $K_T$  (L/g) is the Temkin isotherm constant,  $b_T$  (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, as shown in Fig. 7 The model parameters are listed in Table 2. The Temkin isotherm appears to provide a good fit to the Rhodamine B dye adsorption data.

The adsorption energy in the Temkin model,  $b_T$ , is positive for Rhodamine 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 Rhodamine B dye on ACPLNC can be described reasonably well by the Temkin isotherm.

### Hurkins-Jura adsorption isotherm:

The Hurkins-Jura adsorption isotherm can be expressed as.

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

This can 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 Fig. 8.

### Halsay adsorption isotherm:

The Halsay adsorption isotherm can be given as

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

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 Halsay isotherm constants.

A plot of  $\ln q_e$  Vs  $\ln C_e$ , (is also shown), 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 model parameters are listed in Table 2. This result also shows that the adsorption of Rhodamine B dye on ACPLNC was not based on significant multilayer adsorption. The Halsay model is also not suitable to describe the adsorption of Rhodamine B dye on ACPLNC, because this model also assumes a multilayer behavior for the adsorption of adsorbate onto adsorbent.

### Radlich-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

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

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  $\ln C_e$  (is also shown), 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 ACPLNC decreased with an increase temperature. Furthermore, the value of  $g$  lies between 0 and 1, indicating favorable adsorption.

#### Dubinin-Radushkevich adsorption isotherm:

The Dubinin-Radushkevich adsorption isotherm is another isotherm equation. 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

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

Where,  $Q_D$  is the maximum sorption capacity (mol/g), and  $B_D$  is the Dubinin-Radushkevich constant ( $\text{mol}^2/\text{kJ}^2$ ). 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.

#### Jovanovic adsorption isotherm:

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

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

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 Rhodamine B uptake.

The  $q_{\max}$  is obtained from a plot of  $\ln q_e$  and  $C_e$ . Comparison of the experimental data and Jovanovic model is also shown. 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 Rhodamine B adsorption on the ACPLNC. Both models show a high degree of correlation. This one is clearly confirm the good fit of Langmuir and Temkin models with the experimental data for removal of Rhodamine B dye from the solution.

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

Brunauer–Emmett–Teller (BET) 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 0.05 to 0.30 corresponding to a monolayer coverage lying between 0.50 and 1.50. Its extinction model related to liquid–solid interface is exhibited as:

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

Where,  $C_{\text{BET}}$ ,  $C_s$ ,  $q_s$  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  $C_{\text{BET}}$  and  $C_{\text{BET}} (C_e / C_s)$  is much greater than 1,

In the linear form as used 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 BET model is also shown.

### 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. Each of these models and their linear modes of them equations presented in below.

#### Kinetic Models and Their Linear Forms

Model	Nonlinear Form	Linear Form	Number of Equation
Pseudo-first-order	$dq_t/dt = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	(18)
Pseudo-second-order	$dq_t/dt = k_2(q_e - q_t)^2$	$t/q_t = 1/k_2 q_e^2 + (1/q_e)t$	(19)

Where,  $q_e$  and  $q_t$  refer to the amount of (Rhodamine 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 during 1898 and is used for 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  $k_1$  were 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.

In the pseudo-second order model, 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 5. According to Table 5, the value of  $R^2$  (0.999) related to the pseudo-second order model revealed that (Rhodamine B) dye adsorption followed this model, which is in agreement with the results obtained by Karagoz et al., Hameed et al., and Altenor et al.. Nevertheless, pseudo-first order and pseudo-second order kinetic models cannot identify the mechanism of diffusion of dye into the adsorbent pores.

### The Elovich equation:

The Elovich model equation is generally expressed as

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

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

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

If Rhodamine 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  $\alpha$ ,  $\beta$ , and correlation coefficient ( $\gamma$ ) are summarized in table 6. The experimental data such as the initial adsorption rate ( $\alpha$ ) adsorption constant ( $\beta$ ) and the correlation coefficient ( $\gamma$ ) calculated from this model indicates that the initial adsorption ( $\alpha$ ) 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 ACPLNC adsorbent.

**Thermodynamic parameters:**

Thermodynamic parameters 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 ( $\Delta H$ ), and entropy change ( $\Delta S$ ) may be determined from Van't Hoff equation:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (22)$$

By plotting  $\ln K$  as ordinate and  $1/T$  as abscissa, we will get  $\Delta S$ ,  $\Delta H$  and by using the following equation. We can get the value of have  $\Delta S$ ,  $\Delta H$ .

And by this equation, get the value of  $\Delta G$ .

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots (23)$$

Where,  $\Delta G$  is the free energy change ( $\text{kJ mol}^{-1}$ ),  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $K$  the thermodynamic equilibrium constant and  $T$  is the absolute temperature (K).

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

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

$$2.30 \log \frac{q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (26)$$

$$\log \frac{q_e}{C_e} = \frac{\Delta S}{R \times 2.303} - \frac{\Delta H}{RT \times 2.303} \dots\dots\dots (27)$$

The values of  $\Delta S$ ,  $\Delta H$ ,  $\Delta G$  was obtained from a plot of  $\log (q_e/C_e)$  vs.  $1/T$ .

Heat of reaction ( $-\Delta H$ ) for physical adsorption is reported to be 4.2 to 63 kJ/ mol in literature. The value of  $-\Delta H$  range from -8.89 to -11.543 kJ/mol from Table-6 which indicate that the nature of adsorption of Rhodamine B dye on ACPLNC is physical adsorption. The negative value of  $\Delta H$  &  $\Delta G$  indicate endothermic and spontaneous process of adsorption of Rhodamine B dye on ACPLNC respectively.

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 using modified Arrhenius type equation related to surface coverage ( $\theta$ ) as follows

$$\theta = \left( 1 - \frac{C_e}{C_i} \right) \dots\dots\dots (28)$$

$$S^* = (1 - \theta) e^{-\frac{E_a}{RT}} \dots\dots\dots (29)$$

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  $S^*$  can be calculated from slope and intercept of the plot of  $\ln(1-\theta)$  versus  $1/T$  respectively and are listed in Table 4.

From Table 5 it is clear that the reaction is spontaneous in nature as  $\Delta G^0$  values are negative at all the temperature studied. Again positive  $\Delta H^0$  value confirms that the sorption is endothermic in nature. The positive value of  $\Delta S^0$  reflects the affinities of the adsorbents for the Rhodamine B dye. The result as shown in Table 4 indicate that the probability of the Rhodamine B dye to stick on surface of biomass is very high as  $S^* \ll 1$ , these values confirm that, the sorption process is physisorption.



#### 4. CONCLUSION

The adsorption of Rhodamine B on to Activated Carica papaya leaves carbon was investigated in this research work. The adsorption equilibrium well correlated with both Langmuir and BET isotherm models. The adsorption kinetic process was found pseudo-second-order model. Isotherm and kinetic study indicates that the activated carbon can be effectively employed for the adsorption of Rhodamine B.

#### REFERENCES

- [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" Butterworths: 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] 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.
- [17] 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.
- [18] 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.
- [19] 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.
- [20] Allen, S. J.; Mckay, G.; Khader, K. Y. H. "Intraparticle Diffusions of Basic Dye During Adsorption onto Sphagnum Peat". Environ. Pollut. 1989, 56, 39.

- [21] Weber T W, Chakravorti R K, "Pore and Solid diffusion models for fixed bed adsorbers". J. Am. Inst, Chem. Eng, 1974, 20, 228.
- [22] McKay G, Blair H S, Gardner J R, "Adsorption of dyes on chitin. I. Equilibrium Studies" J. Appl, Polym, Sci. 1982, 27, 3043 – 3057.
- [23] 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.
- [24] Weber W J, Morris J C, "Kinetics of adsorption on Carbon from solution". J, Sanitary Eng, Div. 1964, 90, 79.

TABLE 3: EQUILIBRIUM PARAMETERS FOR THE ADSORPTION OF Rh-B DYE

M <sub>0</sub>	C <sub>e</sub> (Mg / L)				Q <sub>e</sub> (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	4.004	2.402	1.603	1.522	41.99	45.20	46.79	46.96	83.99	90.39	93.59	93.91
50	8.808	8.011	7.240	5.607	82.38	83.98	85.52	88.79	82.38	83.98	85.52	88.79
75	19.28	17.46	15.21	14.10	111.4	115.1	119.6	121.8	74.29	76.72	79.71	81.20
100	28.09	25.69	24.37	22.86	143.8	148.6	151.3	154.3	71.91	74.31	75.63	77.14
125	41.64	40.19	39.31	36.97	166.7	169.6	171.4	176.1	66.69	67.84	68.55	70.42

TABLE 4: LANGMUIR AND FREUNDLICH ISOTHERM PARAMETER FOR THE ADSORPTION OF Rh-B DYE

Model	Constant	Temperature (° C)			
		30	40	50	60
Freundlich	K <sub>f</sub> (mg/g) (L/mg) <sup>1/n</sup>	20.648	30.303	38.315	40.890
	n	1.7399	2.1031	2.4020	2.4054
Langmuir	Q <sub>m</sub> (mg/g)	238.23	212.88	202.53	204.31
	b (L/mg)	0.0534	0.0871	0.1213	0.1417
Temkin	b <sub>T</sub> (J/mol)	52.186	44.255	39.376	40.351
	K <sub>T</sub> (L/mg)	0.5096	0.9929	1.3427	1.4298
Hurkins-Jura	A <sub>H</sub> (g <sup>2</sup> /L)	-2046.7	-2691.3	-3215.4	-3345.7
	B <sub>H</sub> (mg <sup>2</sup> /L)	-1.5401	-1.5316	-1.5223	-1.4846
Halsay	K <sub>Ha</sub> (mg/L)	194.0	1305.5	6356.1	7527.3
	n <sub>Ha</sub>	1.7399	2.1031	2.4020	2.4054
Radlich-Peterson	g	0.4253	0.5245	0.5837	0.5843
	K <sub>R</sub> (L/g)	0.0484	0.0330	0.0261	0.0245
Dubinin-Radushkevich	q <sub>s</sub> (mg/g)	136.18	131.67	131.78	136.99
	K <sub>D</sub> × 10 <sup>-4</sup> mol <sup>2</sup> kJ <sup>-2</sup>	1.6027	1.5863	1.5800	1.5876
Jovanovic	K <sub>J</sub> (L/g)	0.0328	0.0322	0.0314	0.0329
	q <sub>max</sub> (mg/g)	50.475	55.705	60.139	62.569
BET	C <sub>BET</sub> (L/mg)	8.137	15.462	25.918	28.536
	q <sub>S</sub> (mg/g)	0.1229	0.0647	0.0386	0.0350

TABLE 5: DIMENSIONLESS SEPERATION FACTOR ( $R_L$ ) FOR THE ADSORPTION OF Rh-B DYE

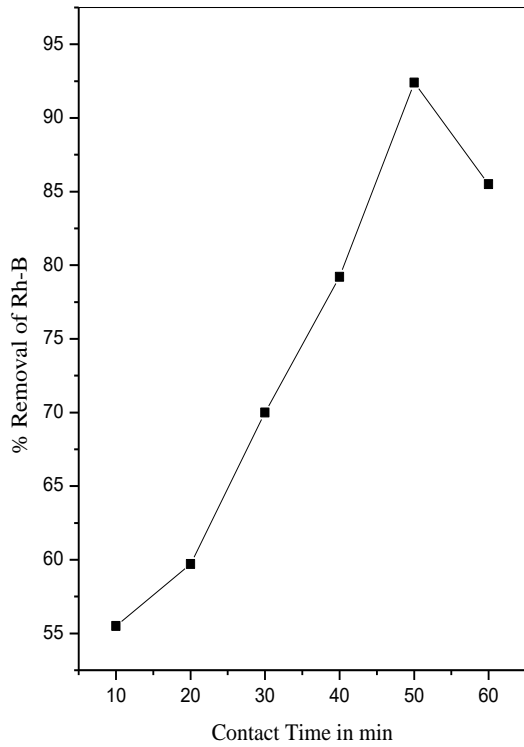
$(C_i)$	Temperature °C			
	30°C	40°C	50°C	60°C
25	0.4282	0.3147	0.2479	0.2201
50	0.2724	0.1868	0.1415	0.1237
75	0.1998	0.1328	0.0990	0.0860
100	0.1577	0.1030	0.0761	0.0659
125	0.1303	0.0841	0.0618	0.0534

TABLE 6: THERMODYNAMIC PARAMETER FOR THE ADSORPTION OF Rh-B DYE

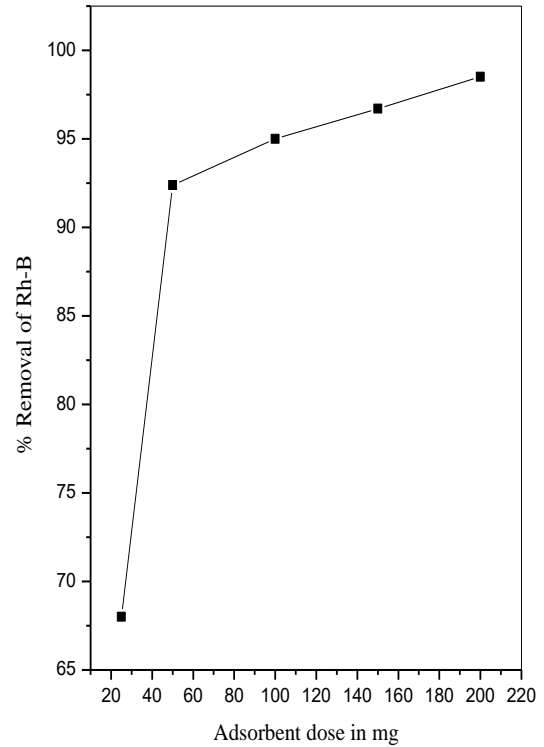
$(C_0)$	$\Delta G^\circ$				$\Delta H^\circ$	$\Delta S^\circ$	$E_a$	$S^*$
	30°C	40°C	50°C	60°C				
25	-4174.5	-5832.9	-7198.1	-7575.7	31.102	117.29	27963.2	0.0000022
50	-3885.9	-4310.8	-4769.1	-5728.2	14.149	59.189	12123.4	0.0015
75	-2672.8	-3103.5	-3675.1	-4051.4	11.6137	47.136	9046.67	0.0071
100	-2367.6	-2763.8	-3041.2	-3367.3	7.5638	32.858	5641.86	0.0297
125	-1748.6	-1942.9	-2092.9	-2401.6	4.6146	20.947	3162.62	0.0954

TABLE 7: THE KINETIC PARAMETERS FOR THE ADSORPTION OF Rh-B DYE

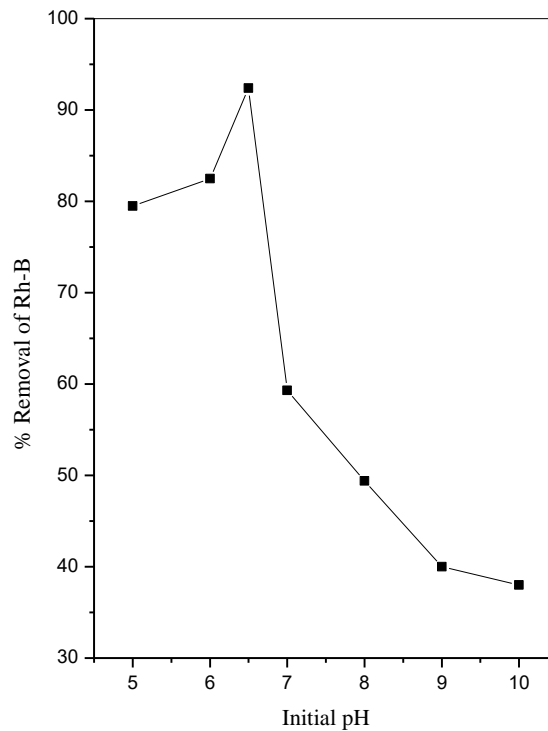
$C_0$	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		$q_e$	$k_2$	$\gamma$	$h$	$\alpha$	$\beta$	$\gamma$	$K_{id}$	$\gamma$	$C$
25	30	52.89	0.0011	0.9904	2.943	70.49	0.0897	0.9896	0.3388	0.9965	1.3096
	40	49.64	0.0028	0.9896	6.951	84.02	0.1495	0.9916	0.1676	0.9892	1.6504
	50	49.38	0.0050	0.9924	12.08	23.21	0.2239	0.9956	0.1031	0.9911	1.7828
	60	49.38	0.0053	0.9935	12.91	40.22	0.2360	0.9926	0.0971	0.9901	1.7953
50	30	94.68	0.0009	0.9957	8.241	37.30	0.0625	0.9960	0.2315	0.9948	1.4868
	40	95.18	0.0010	0.9924	9.462	51.90	0.0655	0.9906	0.2137	0.9901	1.5305
	50	96.08	0.0012	0.9950	11.19	77.60	0.0687	0.9926	0.1959	0.9891	1.5768
	60	97.37	0.0014	0.9967	13.25	15.57	0.0758	0.9896	0.1691	0.9911	1.6376
75	30	122.2	0.0010	0.9907	15.41	21.27	0.0623	0.9906	0.1637	0.9951	1.5627
	40	127.7	0.0011	0.9898	18.46	20.87	0.0573	0.9967	0.1694	0.9891	1.5830
	50	134.5	0.0009	0.9890	17.08	11.99	0.0492	0.9952	0.1933	0.9911	1.5581
	60	132.6	0.0014	0.9892	24.96	35.86	0.0579	0.9968	0.1574	0.9891	1.6353
100	30	159.5	0.0010	0.9911	25.86	19.84	0.0425	0.9942	0.1840	0.9932	1.5394
	40	164.3	0.0010	0.9920	25.83	20.89	0.0417	0.9901	0.1825	0.9901	1.5527
	50	166.2	0.0010	0.9941	28.52	27.21	0.0427	0.9931	0.1737	0.9956	1.5771
	60	169.2	0.0010	0.9952	29.71	31.10	0.0428	0.9963	0.1696	0.9912	1.5928
125	30	184.9	0.0006	0.9939	19.81	14.80	0.0363	0.9909	0.1930	0.9914	1.4607
	40	188.3	0.0006	0.9960	20.20	15.27	0.0357	0.9969	0.1924	0.9901	1.4697
	50	188.4	0.0006	0.9907	22.08	21.86	0.0378	0.9956	0.1779	0.9911	1.5007
	60	194.2	0.0005	0.994	21.40	17.81	0.0354	0.9926	0.1869	0.9943	1.4945



Fig;2- Effect of Contact Time on the Removal of Rh-B  
[Rh-B]=50 mg/L;Temperature 30°C;Adsorbent dose=50mg/50ml



Fig;3- Effect of Adsorbent dose on the removal of Rh-B  
[RhB]=50mg/L;Contact Time 60min;Temperature 30°C



Fig;4- Effect of Initial pH on the removal of Rh-B  
[RhB]=50 mg/L;Temperature 30°C;Adsorbent dose=50mg/50ml

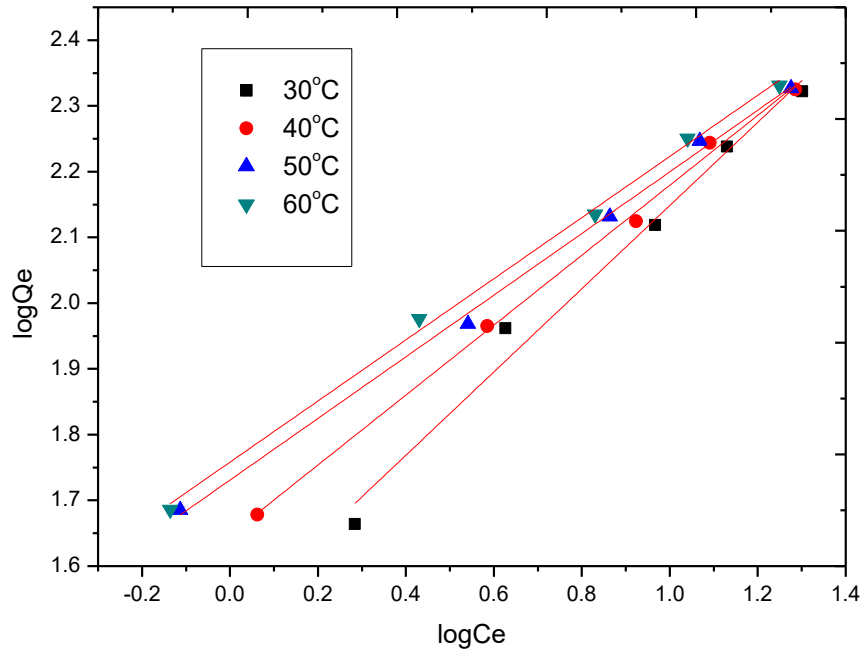


Fig.5 - Freundlich adsorption isotherm

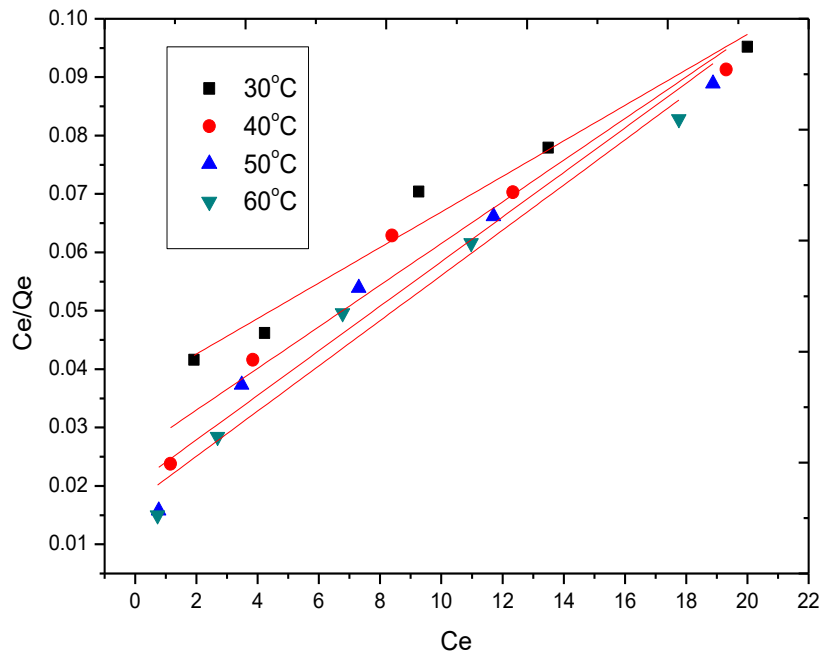


Fig.6 - Langmuir adsorption isotherm

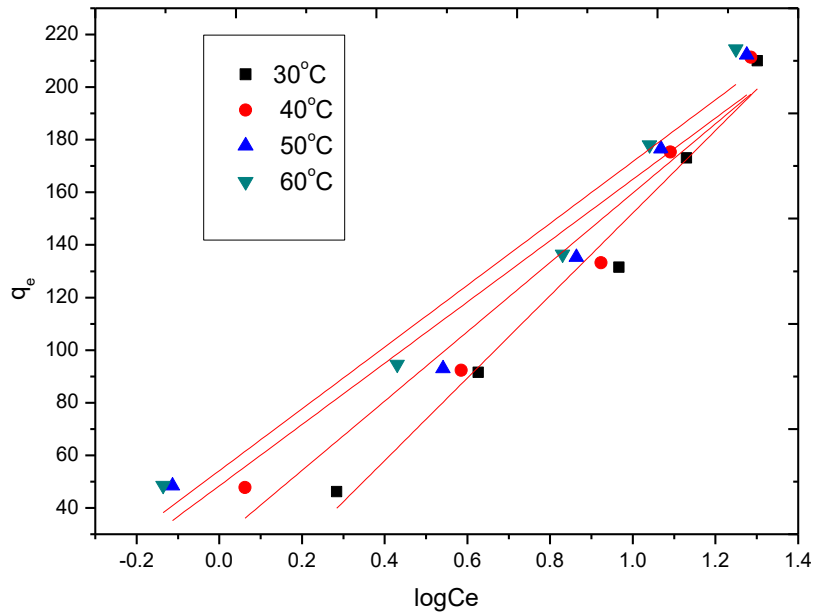


Fig.7 - Temkin adsorption isotherm

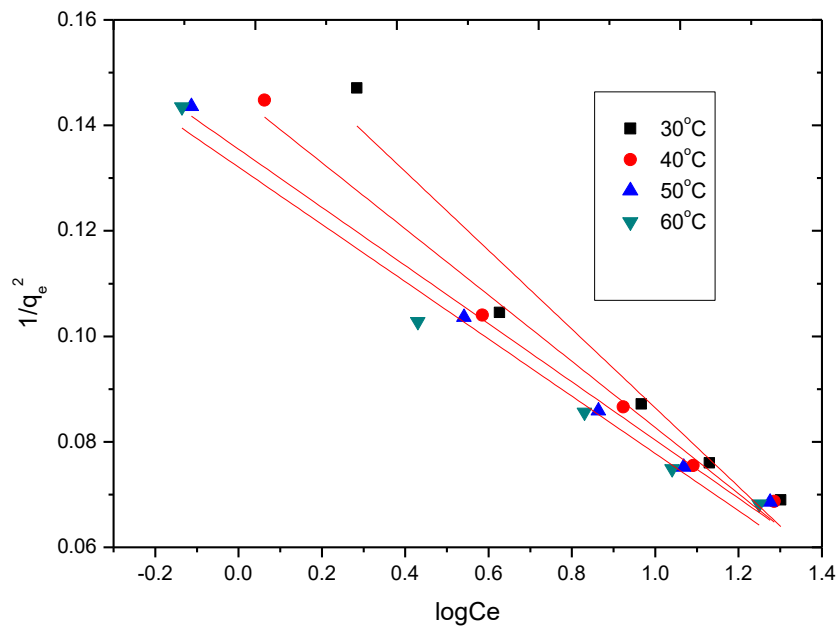


Fig.8 - Hurkins-Jura adsorption isotherm