

## **Adsorption of Acid violet4BS from aqueous solutions on to *Lagerstroemia indica* seeds as a low cost biosorbent**

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**Abstract :** The use of low-cost and ecofriendly adsorbents was investigated as an ideal alternative to the current expensive methods of removing dyes from wastewater. Lagerstroemia indica seeds (LIS) was used as an adsorbent for the removal of Acid violet 4BS from aqueous solutions. The rate of adsorption was investigated under various parameters such as contact time, carbon dosage, pH and temperature for the removal of these dyes. Kinetic study showed that the adsorption of dyes on Lagerstroemia indica seeds (LIS) was a gradual process. Adsorption rate increased with the increase in carbon dosage, temperature and decreases with increase in pH. Pseudo-first-order, the Elvovich equation, pseudo-second order, and intra-particle diffusion models were used to fit the experimental data. The sorption kinetics of Acid violet onto LIS was described by the pseudo-second-order kinetic equation. Intra-particle diffusion process was identified as the main mechanism controlling the rate of the dye sorption. Thermodynamic activation parameters such as  $\Delta G^0$ ,  $\Delta S^0$  and  $\Delta H^0$  were also calculated.

**Keywords :** Adsorption; Acid violet; Pseudo; Intraparticle.

### **1. Introduction**

Water is very essential for our day to day life activities. It can be used for drinking, domestic, agricultural, and industrial purposes. Contamination of the water bodies from a variety of sources has become an increasingly serious problem in recent years. The release of dyes into wastewater by various industries like textiles, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries possess serious environmental problems due to the persistent and recalcitrant nature of the dyes. In addition, some dyes are either toxic or mutagenic and carcinogenic [1]. The conventional methods for treating dyes containing wastewaters are coagulation and flocculation [2], oxidation or ozonation [3],[4] membrane separation[5] and activated carbon adsorption[6]. These methods are costly and cannot be used effectively to treat the wide range of dye wastewaters when compared with adsorption processes. The present investigation is an attempt to remove acid violet by adsorption process.

Adsorption is an important technique in separation and purification process. The objective of this study is to prepare activated carbon from Lagerstroemia indica seed by chemical activation with Potassium Hydroxide. Large availability of this material around our city attracted us to utilize it as potential adsorbent for the removal of toxic dyes. The adsorption capacity of Lagerstroemia indica seed used as the adsorbent for the removal of aqueous organic dyes varying with process factors including initial dye concentration, contact time, initial pH, adsorbent dose and temperature.

## 2. Experimental

### 2.1 Adsorbent preparation

The Lagerstroemia indica seeds (LIS) used in this study was collected from local fields. The collected seeds were extensively washed with tap water to remove soil and dust, sprayed with distilled water then dried, charred with excess quantity of potassium hydroxide for 10h. Then the resultant carbon is washed with excess quantity of distilled water and dried at 110°C for 1 hour and stored in a tight lid container for further studies. It is then screened through a mesh sieve with a particle size range of 180-300 µm.

### 2.2 Preparation of dye solution

The dye (Acid violet), in commercial purity, was used without further purification. The dye stock solutions were prepared by dissolving 1g of accurately weighted dye in distilled water to the concentration of 1000 mg/L. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

### 2.3 Adsorption dynamics

In order to predict the mechanism of the present biosorption process and evaluate the performance of the biosorbent for dye removal, three well-known kinetic models were used to fit the experimental data; pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

#### 2.3.1. Lagergren model

For a batch contact time process, where rate of sorption of dye on to given adsorbent is proportional to amount of dye sorbed from solution, first order Lagergren kinetic equation may be expressed as [7],

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

where,

$q_e$  = amount of dye adsorbed at equilibrium (mg/g),

$q_t$  = amount of dye adsorbed at time  $t$  (mg/g) and

$k_1$  = rate constant for first order adsorption ( $\text{min}^{-1}$ ).

Hence a linear trace is obtained between the two values  $\log(q_e - q_t)$  and  $t$ , provided the adsorption follows first order kinetics. In order to examine the efficiency of an adsorbent, this study is useful in removal of adsorbate species from aqueous solution by an adsorbent.

#### 2.3.2 Pseudo second order model

To describe dye adsorption, modified pseudo second order equation is expressed as follows [8]

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

Where,

$q_e$  = amount of dye adsorbed at equilibrium (mg/g),

$q_t$  = amount of dye adsorbed at time  $t$  (mg/g) and

$k_2$  = rate constant for pseudo second order adsorption, (g/mg/min).

For the boundary conditions  $t=0$  to  $t=1$  &  $q_t = 0$ ,  $q_t = q_t$

Integrated form of equation is as follows,

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (3)$$

Linear form of equation can be expressed as follows,

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

Thus a plot of  $t / q_t$  vs  $t$  of above equation should give a linear relation with a slope of  $1 / q_e$  and an intercept of  $1 / k_2 q_e^2$

## 2.4 Isotherm models

Sorption isotherms define the equilibrium relationship between sorbent and sorbate. In other words, how the sorbed molecules interact with sorbents when the sorption process approaches to an equilibrium state can be described by sorption isotherms [9]. Sorption isotherms also ensure many fundamental physicochemical data to estimate the applicability of sorption processes. Sorption isotherms are characterized by certain constants which values express the surface properties and affinity of the sorbent and can also used to find the sorptive capacity of a mass [10]. Different isotherm models are available, and three of them are selected in this study: Langmuir, Freundlich and tempkin models, due to their simplicity and reliability.

### 2.4.1 Langmuir isotherm

The study of Langmuir isotherm is essential in assessing the adsorption efficiency of adsorbent. This model was based on assumption of formation of monolayer of adsorbate species onto the surface of adsorbent. This study is useful in optimizing the operating condition for effective adsorption. Langmuir equation is [11-13],

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot b} + \frac{C_e}{Q_0} \quad (5)$$

where,

$q_e$  = amount of dye adsorbed at equilibrium (mg/g),

$C_e$  = equilibrium constant of dye (mg/L),

$Q_0$  = Langmuir Constant related to adsorption capacity (mg/g) and

$b$  = Langmuir Constant related to energy of adsorption capacity (L/mg)

The values  $Q_0$  and  $b$  at different temperatures were determined from slopes and intercepts of the plot of  $C_e / q_e$  Vs  $C_e$ . Equilibrium parameter  $R_L$  is represented as follows [14]

$$R_L = \frac{1}{1 + b \cdot C_0} \quad (6)$$

$C_0$  is initial dye concentration (mg/L)

$R_L$  values between 0&1 indicate favourable adsorption for all initial concentration and temperature studied.  $R_L$  indicates isotherm shape and whether it is favourable or not as per the criteria given subsequently.

$R_L$ values	Adsorption
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

### 2.4.2. Freundlich isotherm

At equilibrium conditions, adsorbed amount  $q_e$  can be predicted by using Freundlich equation[15],

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (7)$$

Where,

$q_e$  = dye concentration in solid at equilibrium (mg/g),

$C_e$  = dye concentration in solution at equilibrium, (mg/L),

$k_f$  = measure of adsorption capacity and

$n$  = adsorption intensity.

A plot of  $\log q_e$  Vs  $\log C_e$  gives a slope of  $1/n$  and intercept of  $\log k_f$ .

## Results and Discussion

### 3.1. Effect of initial dye concentration

The initial concentration of acid violet solution was varied from 10, 20, 30 and 40 mg/L and batch experiments were carried out with 100 mg of the adsorbent at 30°C and at pH 7.0. An decreased percentage removal of acid violet from 75.00 to 46.15% observed with 100 mg of the adsorbent in agitation time of 90 minutes and results are shown in Figure 1. In order to establish equilibration time for maximum uptake and to know the kinetics of adsorption process, the adsorption of acid violet on adsorbent was studied as a function of contact time. It was found that time of equilibrium as well as time required to achieve a definite fraction of equilibrium adsorption is dependent of initial concentration.

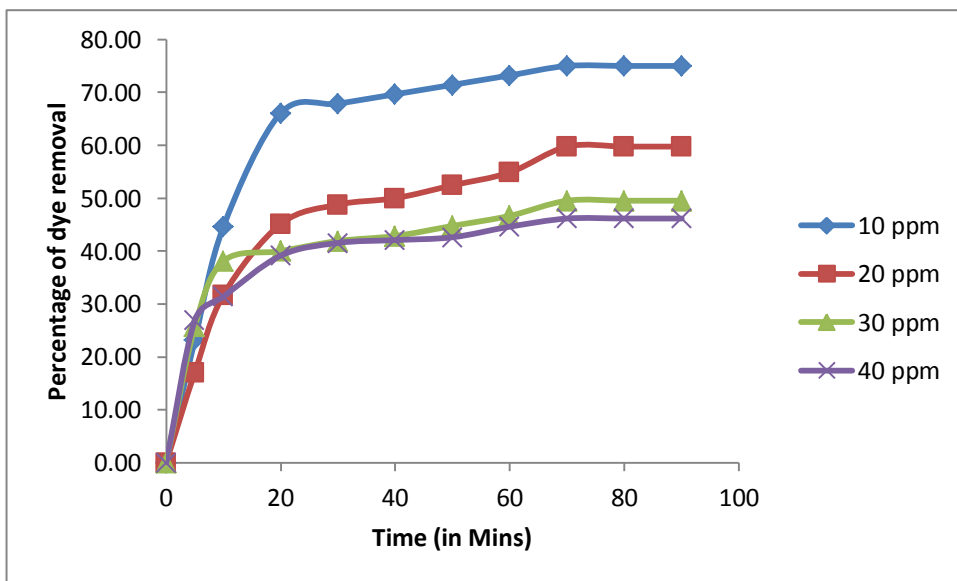
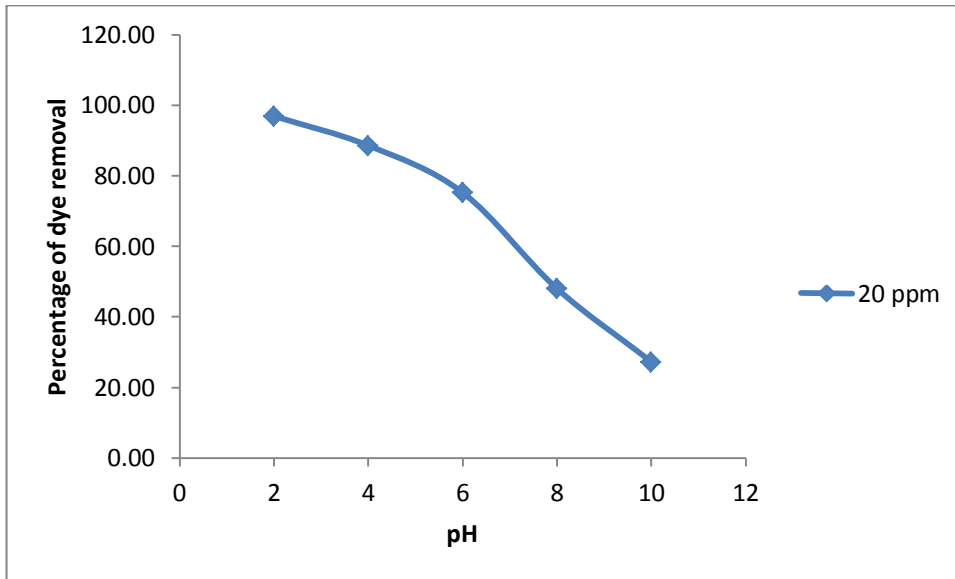


Figure1. Effect of agitation time on adsorption –initial concentration variation

### 3.2 Effect of pH

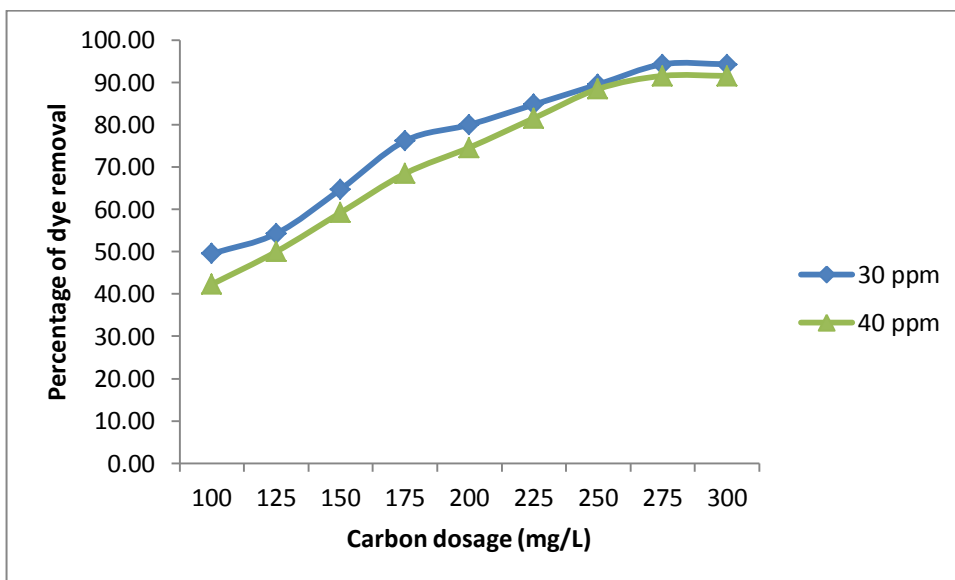
The effect of pH for the adsorption of acid violet on to LIS over a Ph range of 2 to 10 is represented in Figure 2. The uptake of acid violet decreased from  $96.92 \text{ mg g}^{-1}$  to  $27.27 \text{ mg g}^{-1}$  when the solution pH was increased from 2 to 10. The maximum uptake of acid violet by LIS was obtained at pH 2.0. At pH 2.0 a significantly high eletrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favour the adsorption of dye anions due to the electrostatic repulsion [16, 17]. Also, lower adsorption of acid violet at alkaline pH is due to the presence of excess OH ions competing with the dye anions for the adsorption sites. At alkaline pH significant adsorption of the anionic dye on the adsorbent still occurred. This suggests that the second mechanism, i.e. chemisorption, might be operative.



**Figure 2.** Effect of pH on removal of Acid violet dye solution

### 3.3 Effect of adsorbent dose

The effect of carbon dosage on the percentage of dye removal with two different initial dye concentrations (30 mg/L, 40 mg/L) at various carbon dosages of 125 mg to 300 mg were presented in Figure 3. The percentage of adsorption increased as the adsorbent concentration increased and attain equilibrium beyond 300 mg. The increase in the percent removal of dyes with the increase in adsorbent dosage is due to the availability of larger surface area with more active functional groups at higher adsorbent dosages and saturation occurs as a result of non-availability of active sites on the adsorbent.



**Figure 3.** Percentage of Acid violet removed by LIS at various carbon dosages

### 3.4. Adsorption kinetics

#### 3.4.1. First order kinetics

Lagergren first order plot for the adsorption of acid violet at various initial concentrations is given in the Figure 4. The applicability of Lagergren model suggests the formation of a monomolecular layer of dye

species onto surface of adsorbent. The study of influence of initial dye concentration on Lagergren rate constant from Table 1 shows a decrease in rate constant with increase in initial dye concentration.

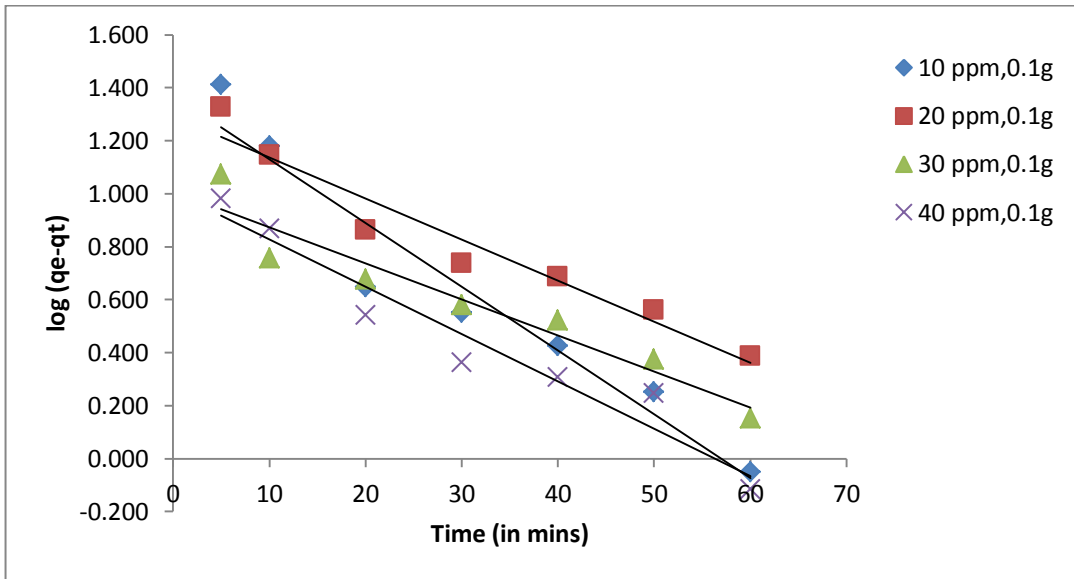


Figure 4. First order plot of acid violet initial concentration variation

### 3.4.2. Pseudo second order model

Figure 5 shows that pseudo second order equation at various initial dye concentrations (10, 20, 30 & 40 mg/L). These plots show that data had good correlation coefficients when pseudo second order equation was employed and was possible to ascertain from them whether rate determining process is a chemical reaction. Thus increasing dye concentration from 10 to 40 mg/L, equilibrium sorption capacity  $q_e$  decreases acid violet sorbed at any contact time increases.

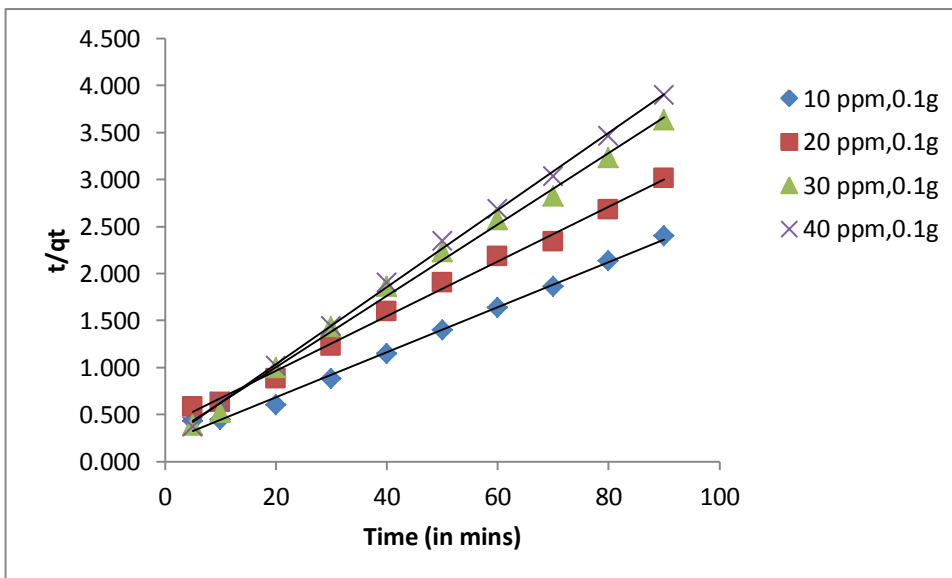


Figure 5. Pseudo Second order plot of acid violet initial concentration variation

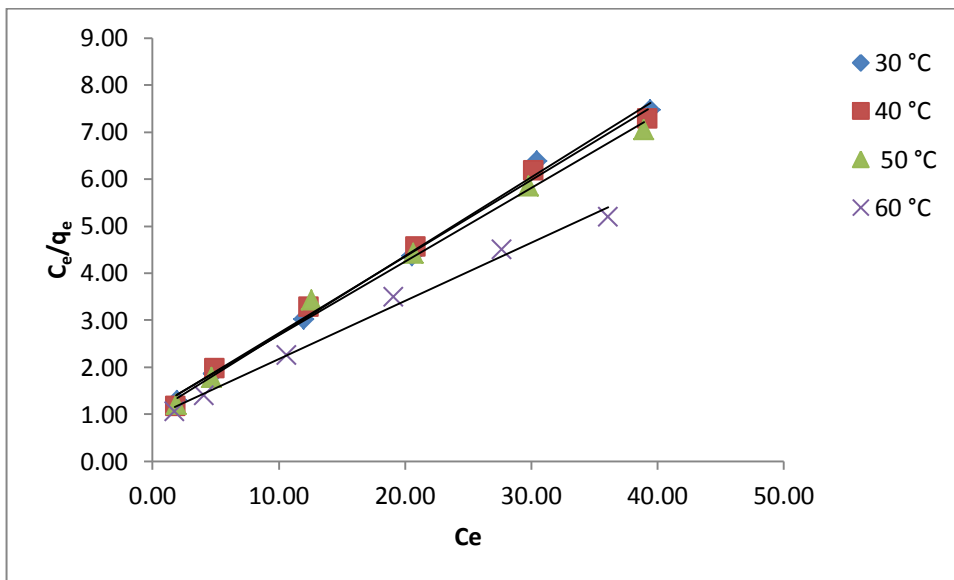
**Table 1. Kinetic model values for adsorption of acid violet onto activated LIS carbon**

Concentration (ppm)	Pseudo first order kinetics			Pseudo second order kinetics		
	$K_1 \times 10^{-2} (\text{min}^{-1})$	$q_{e,cal} (\text{mg/L})$	$R^2$	$K_2 \times 10^{-3} (\text{min}^{-1})$	$q_{e,cal} (\text{mg/L})$	$R^2$
10	3.66	24.53	0.9355	$2.2111 \times 10^{-3}$	45.45	0.9974
20	3.64	24.83	0.9779	$2.7507 \times 10^{-3}$	42.19	0.996
30	3.09	20.01	0.9395	$2.2391 \times 10^{-3}$	44.44	0.9975
40	3.39	15.43	0.9859	$4.5390 \times 10^{-3}$	40.32	0.9976

### 3.5. Isotherm modeling

#### 3.5.1. Langmuir Adsorption Isotherm

Adsorption isotherm obtained by fixing adsorbent dosage of 100 mg and 100 minutes of agitation time is shown in the Figure 6. The result of Langmuir adsorption isotherm for the selected adsorbent/adsorbate system is given in the Table 2. The adsorption capacity  $Q_0$  values found to be comparable with commercial activated carbon. The values of  $R_L$  obtained in this study indicate the applicability of Langmuir adsorption isotherm. The calculated value  $R^2$  confirm the applicability of Langmuir adsorption isotherm.



**Figure6. Langmuir plots for the adsorption of acid violet**

#### 3.5.2. Freundlich adsorption isotherm

Freundlich plot for the adsorption of acid violet on to LIS activated carbon is given in the Figure 7 and the results of Freundlich plot are given in the Table 2. It shows that the values of adsorption intensity  $1/n > 1$  reveal that applicability of Freundlich adsorption is not good compared to Langmuir Adsorption Isotherm. Study of temperature effects on Freundlich parameters reveals increasing trend in adsorption capacity with increase in temperature.

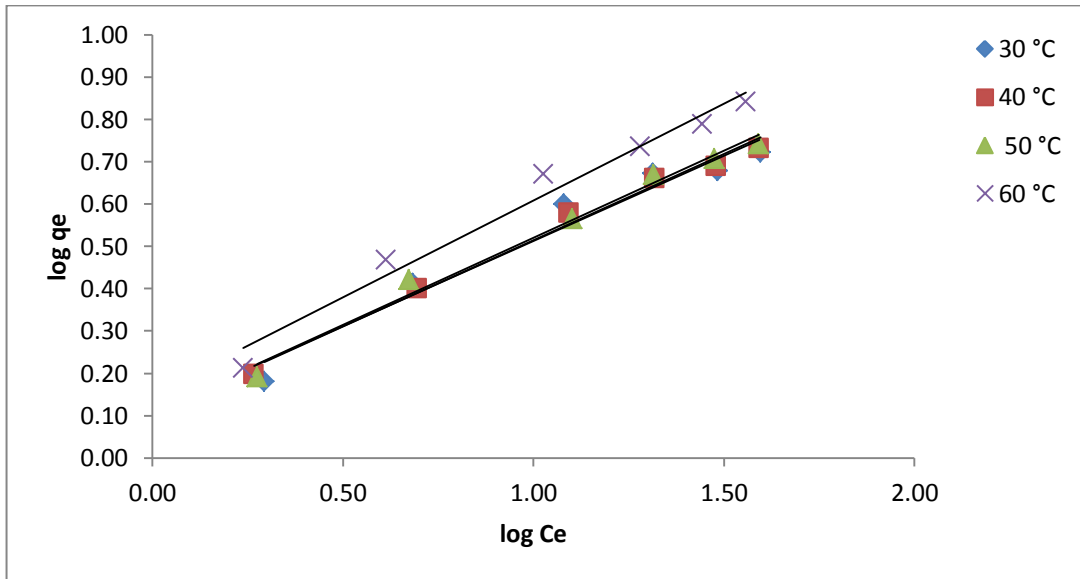


Figure 7.Freundlich plots for the adsorption of acid violet

### 3.5.3. Temkin isotherm

The derivation of Temkin isotherm assumes that the fall in heat of sorption is linear rather than logarithmic as implied in Freundlich equation. Heat of sorption of all the molecules in the layer would decrease linearly with coverage due to sorbate / sorbent interaction.

The linear form of the Temkin isotherm [18, 19] can be expressed as,

$$q_e = B \ln A + B \ln C_e \tag{8}$$

where,  $C_e$  = concentration of the dye at equilibrium (mg/L),  $q_e$  = amount of dye adsorbed at equilibrium (mg/g) and A plot of  $q_e / \ln C_e$  is used to determine the constants A, B are listed in the table 2.

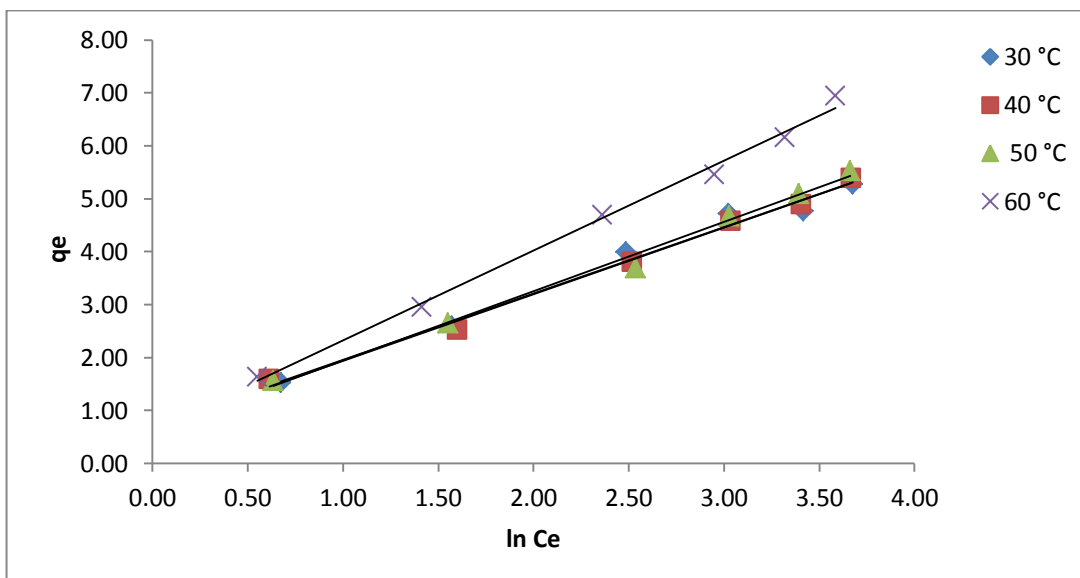


Figure 8.Temkin plots for the adsorption of acid violet



**Table 2 Results of various plots for the adsorption of acid violet on to LIS**

Temperature(°C)	Langmuir			Freundlich			Tempkin		
	Q <sub>o</sub>	b (L/mg)	R <sup>2</sup>	n	K <sub>f</sub>	R <sup>2</sup>	B	A	R <sup>2</sup>
30	5.81	0.1772	0.9981	1.4472	2.1984	0.9912	1.7189	0.593	0.9818
40	6.19	0.1750	0.9997	1.3609	2.2039	0.9867	1.9339	0.5192	0.9866
50	6.41	0.2069	0.9992	1.4968	1.5707	0.9809	1.9341	0.5863	0.9916
60	9.25	0.0665	0.9999	1.6941	1.1700	0.9806	1.9308	0.6867	0.9939

### 3.6. Adsorption thermodynamics

The thermodynamic parameters such as change in Gibbs energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) were determined using the following equations [20]:

$$K_c = C_A / C_S \quad (9)$$

$$\ln K_c = (\Delta S^0 / R) - (\Delta H^0 / RT) \quad (10)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (11)$$

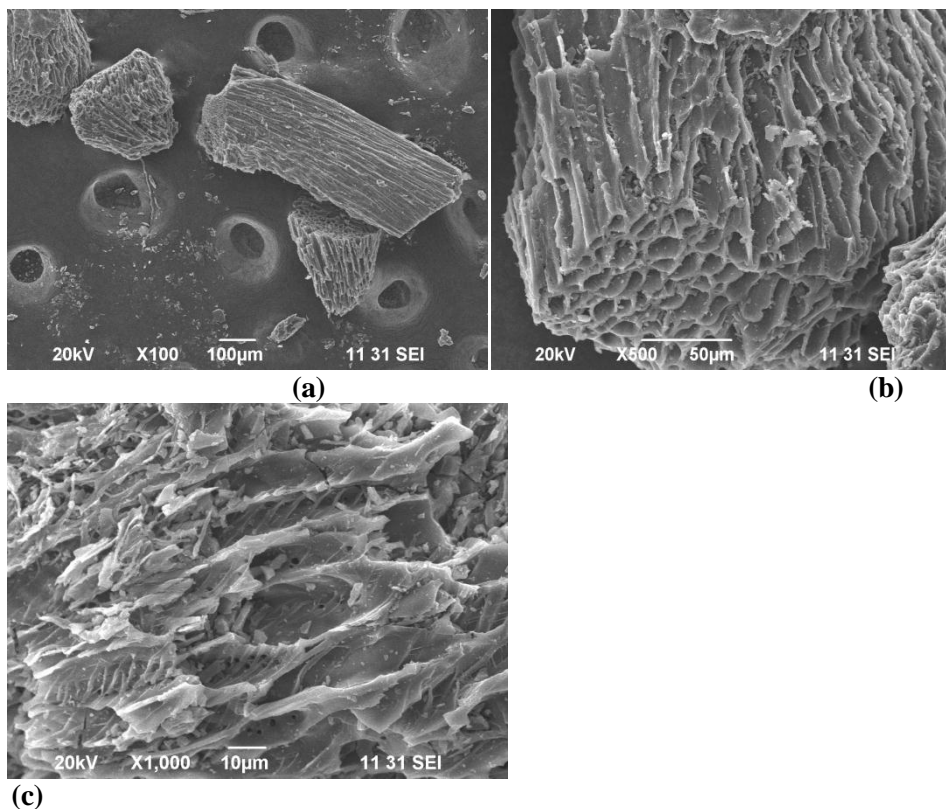
where R (8.314 J/mol K), T (K), C<sub>A</sub>, C<sub>S</sub> and K<sub>c</sub> (L/g) are the gas constant, the absolute temperature, the amount of dye adsorbed on the adsorbent of the solution at equilibrium (mol/L), the equilibrium concentration of the dye in the solution (mol/L) and the standard thermodynamic equilibrium constant, respectively. By plotting a graph of ln K<sub>c</sub> versus 1/T, the values  $\Delta H^0$  and  $\Delta S^0$  can be estimated from the slopes and intercepts, respectively. Table 3 shows the negative values of  $\Delta G^0$  and positive  $\Delta H^0$ . Data indicate that the Acid violet 4BS adsorption processes are endothermic processes. The positive value of  $\Delta S^0$  suggests increased randomness at the solid/solution interface occurs in the internal structure of the adsorption of Acid violet 4BS dye onto LIS. The positive values of  $\Delta H^0$  indicate the presence of an energy barrier in the adsorption process and endothermic process [21].

**Table 3 Thermodynamic parameters of dye adsorption on LIS**

Temperature (°C)	Thermodynamic parameters		
	$\Delta G^0$ (kJ/mol)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol/K)
30	-18.34		
40	-19.20	40.1	20.1
50	-19.83		
60	-20.61		

### 3.7. SEM analysis

Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent surface. It is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent. Scanning electron micrographs of raw LIS are shown in Fig.9. From Fig.9, it is clear that LIS has considerable numbers of pores where, there is a good possibility for dyes to be trapped and adsorbed into these pores. The SEM of LIS samples show very distinguished dark spots which can be taken as a sign for effective adsorption of dye molecules in the cavities and pores of this adsorbent.



**Figure 9. SEM image of Activated Carbon**

### 3. Conclusion

The present study showed that Lagerstroemia indica seed (LIS) activated carbon modified with KOH can be used as an effective adsorbent for the removal of acid violet dye from aqueous solution. The maximum adsorption capacity was obtained (96.92%) by using carbonaceous Lagerstroemia indica seed at pH 2 with adsorbent dose of 100 mg and with agitation time of 90 minutes. The adsorption followed pseudo second order kinetics and data fitted the Langmuir and Freundlich adsorption isotherms. Thermodynamics studies indicated that the dye adsorption onto LIS was as spontaneous, endothermic, and chemical reaction.

Based on the data of present study, LIS is an eco-friendly adsorbent for dye removal from colored textile wastewater.

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