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Adsorption Studies of an Acid Dye From Aqueous Solution Using Lagerstroemia Indica Seed Activated Carbon as an Adsorbent

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***Abstract**: The effectiveness of adsorption for acid dye removal from wastewaters has made it an ideal alternative to other expensive treatment options. The removal of acid Violet 4BS onto seeds of Lagerstroemia indica (LIS) from aqueous solutions was investigated using parameters such as contact time, pH, temperature, adsorbent doses, and initial dye concentration. Adsorption isotherms of dyes onto LIS were determined and correlated with common isotherm equations such as the Langmuir and Freundlich models. It was found that the Langmuir isotherm appears to fit the isotherm data better than the Freundlich isotherm. Parameters of the Langmuir and Freundlich isotherms were determined using adsorption data. The maximum removal of Acid Violet 4BS by the adsorbent was obtained at pH 2. The maximum percentage of dye removal (86.67%) was obtained at an initial dye concentration of 10mg/L with adsorbent dosage of 50 mg per 50 ml of dye solution. The adsorption kinetics of acid violet 4BS could be described by the pseudo-second order reaction model. The data obtained from adsorption isotherms at different temperatures were used to calculate several thermo-dynamic quantities such as the Gibbs energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) of adsorption. The adsorption process was found to be spontaneous, exothermic and physical in nature. Locally available adsorbent LIS was found to have a low cost and was promising for the removal of acid violet 4BS from aqueous solutions.*

***Keywords:** Acid dye, Adsorption, Freundlich isotherm, Langmuir isotherm, Low-cost materials;*

I. INTRODUCTION

Wastewater generated as a result of domestic, industrial and agricultural activities often contains various regulated compounds, both organic and inorganic in nature. Effluents from industries such as dyeing, paper and pulp, textile, etc. contain many dyes which are toxic and need to be removed [1].Dye contamination in wastewater can lead to a variety of environmental problems. Colored water can affect plant life and thus an entire ecosystem can be destroyed by contamination of various dyes in water. With the growing emphasis on environmentally friendly industry, it is important to discover cheap and efficient methods of cleaning industrial wastewater. Activated carbon has many applications, one of which is used as an efficient and versatile adsorbent for purification of water, air and many chemical and natural products [2]. This is possible due to the highly porous nature of the solid and its extremely large surface area to volume ratio. Much of this surface area is contained in micropores and mesopores. Currently, activated carbon has been an effective adsorbent for dye removal [3–5]. The adsorption capacity of a certain carbon is known to be a function of porous structure, chemical nature of the surface, and pH of the aqueous solution. In addition, the adsorption process is influenced by the nature of the adsorbate and its substituent groups. The presence and concentration of surface functional groups plays an important role in the adsorption capacity and the removal mechanism of the adsorbates [6]. It is also known that acid treatment can modify the carbon physical and chemical properties, influencing their adsorption behavior [7]. In the present study, LIS have been used as an adsorbent for the removal of acid dye from aqueous solutions. Acid violet selected as the model compound in order to evaluate the capability of LIS to remove dye from wastewaters. In order to evaluate the adsorption capacity of LIS, contact time, temperature, pH, adsorbate doses, initial dye concentration, kinetics, thermodynamics, and isotherm studies were conducted.

II. MATERIALS AND METHODS

2.1. Carbon preparation and characterization

In the present study, Lagerstroemia Indica Seed (LIS) was used for the preparation of activated carbon. The seeds were collected from in and around Erode Town, Tamilnadu, India which were available in abundent. The collected seeds were dried and allowed to chemical activation, by the addition of 1:1 hydrochloric acid and

heated to boiling for about 3 hours. The charred material was filtered and washed with water to remove the residual acid from pores of the carbon. The material was then washed with distilled water, until the pH of the adsorbent reached 7±0.2. Then it was dried and carbonised at 400°C for one hour in a muffle furnace. The carbon was ground well and sieved to get a particle size of 300µm. The sieved adsorbent was activated at 800ºC and stored in an airtight container for further experiments. Characteristics of the adsorbent such as moisture content, ash content, conductivity, surface area, bulk density, specific gravity, iodine number, water soluble and HCL soluble matter were determined. The results are summarized in Table 1. The dye used for the adsorption study in the present work was Acid Violet 4BS. It has a molecular weight of 483 with C.I. 42640. The λmax value of the dye was 550nm.

2.2. Adsorption experiments

2.2.1. Effect of pH

The effect of pH on the amount of dye removal was analyzed over the pH range from 2 to 10. The pH was adjusted with 0.1 N NaOH and HCl solution by using a pH meter. In this study, 50 ml of dye solution of 40 mg/l was agitated with 50mg of LIS using mechanical shaker at room temperature (308 K). Agitation was made for 45 min, which is more than sufficient time to reach equilibrium at a constant agitation speed of 150 rpm. The samples were then centrifuged and the concentration left out in the supernatant dye solution was analyzed by using a UV spectrophotometer.

2.2.2. Effect of adsorbent dosage and of initial dye concentration

The effect of LIS mass and initial dye concentration on the amount of dye adsorbed was investigated by putting 50 ml of dye solution of different initial dye concentrations (10, 20, 30, 40 mg/l) in contact with different weights (25, 50, 75, 100 mg) of LIS, using water-bath shakers at room temperature (303 K) for 45 min.

2.2.3. Isotherm studies

The adsorption of acid violet from aqueous solution onto LIS was performed using the batch equilibrium technique. For the determination of adsorption isotherms, 50 ml of dye solution of known concentration was shaken with 100 mg of the adsorbent using mechanical shakers at different temperatures (303, 313, 323 and 333 K). Initial dye concentrations were changed in the range of 5 to 50 mg/l. The mixture was allowed to settle and then was centrifuged at 2500 rpm for 10 min. The equilibrium concentrations of dyes were measured with a UV spectrophotometer at appropriate wavelength corresponding to the maximum absorbance of 550nm of acid violet respectively.

III. RESULTS AND DISCUSSION

3.1 Effect of agitation time and initial dye concentration

The effect of agitation time on the removal of Acid Violet 4BS dye by LIS at various initial dye concentrations (10 to 40 mg/L) were presented in Fig 4.1. The amount of dye adsorbed at various intervals of time indicates that the removal of dye initially increases with time but attains equilibrium within 80 minutes for all concentrations. The adsorption process was found to be very rapid initially and a large fraction of the total concentration of dye was removed in the first 5-10 minutes and then it proceeds slowly until equilibrium is reached. This may be due to the increase in the number of vacant surface sites available at initial stage. The curves were single, smooth and continuous till the saturation of the dye on the carbon surface. As the initial dye concentration increased, there was a considerable reduction in the percentage of dye removal.

3.2 Effect of initial dye concentration and adsorbent dosage

The effect of initial dye concentration and adsorbent dosage results were summarized in Table.2. From the results it is evident that even though the percentage of dye removal increases with increase in adsorbent dosage at various initial dye concentrations, the amount of dye removed (mg/g) decreases with increase in adsorbent dosage. The maximum amount of dye removal takes place at an initial dye concentration of 20 mg/L with a carbon dosage of 25 mg per 50 ml of dye solution.

3.3 Analysis of Adsorption Kinetics

The study of adsorption kinetics is important in describing the adsorption process as it explains how fast the process occurs and also provides information on the factors affecting or controlling the adsorption rate. Various models can be used to analyse the kinetics of the adsorption process. The pseudo first-order and second-order kinetic equations of Largergren are the most widely used for the adsorption of solutes from a liquid solution. The linear form of equations for the pseudo first-order and second-order kinetic models can be represented by

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{and} \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (1)$$

Where q_t and q_e are the amount of dye adsorbed (mg/g) at time t (min) and equilibrium time.

The Lagergren plot of pseudo first order and pseudo second order plot were presented in Fig. 4.2 and Fig. 4.3. A comparison of the kinetic parameters estimated from pseudo first-order and pseudo second – order equations are presented in Table 3, it is evident that R^2 values for the pseudo second –order model is higher than the pseudo first-order model. This shows that the adsorption of Acid Violet 4BS on Lagerstroemia Indica seed (LIS) activated carbon is well-fitted to the pseudo second-order kinetics model compared to the pseudo first-order model. The table shows that the experimental data and the correlation co-efficient for the second-order kinetic model are better represented the adsorption kinetics, suggesting that the adsorption process was controlled by chemisorptions.[8]

3.4 Intra particle diffusion studies

Adsorption is a multi-step process involving transport of solute molecules from the aqueous phase to the surface of the solid particles and then diffusion of the solute molecules into the interior of the pores which is likely to be a slow process, and is therefore, rate determining. Webber and Morris provided the rate, q_t , for intra-particle diffusion by

$$q_t = k_d t^{\frac{1}{2}} \qquad (2)$$

Where q_t is the amount of dye adsorbed (mg/g) at any time t, and k_d $(mg/g.min.)$ the rate constant for intra-particle diffusion. The plot of q_t against $t^{\frac{1}{2}}$ may present a multi-linearity correlations, which indicates that two or more steps occur during adsorption process. The value of K_d obtained from the slope of the plot of q_t against $t^{1/2}$ is shown in Fig 4.4, that the sorption process tends to be followed by two phases. The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds by surface sorption and intraparticle diffusion. The initial curved portion of the plot indicates a boundary layer effect while the second linear portion is due to intraparticle diffusion. The slope of the second linear portion of the plot has been defined as the intra-particle diffusion parameter K_d. On the other-hand, the intercept of the plot reflects the boundary layer effect. The calculated intra-particle diffusion coefficient K_d values was given by 3.313,2.351,2.545 and 0.801 mg/g min for initial dye concentrations of 10,20,30, and 40 mg/L at 30^0c.

3.5 Adsorption isotherms

Langmuir Isotherm

Langmuir isotherm can be applied for the adsorption of dye onto carbon[9]

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (3)$$

Where, C_e is the equilibrium concentration (mg/L), q_e is the amount of dye adsorbed (mg/g), Q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The linear plot of $\frac{C_e}{q_e}$ vs. C_e shows that the adsorption follows Langmuir isotherm models. The value of Q_0 and b were calculated from the slope and intercept of the plot respectively. The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless separation factor of equilibrium parametersR_L. It can be defined by,

$$R_L = \frac{1}{1 + bC_o}$$

Where C_o is the initial dye concentration (mg/L) and b is the Langmuir constant (L/mg).

Freundlich isotherm

The Freundlich equation is widely used in environmental engineering practice to model adsorption of pollutants from an aqueous medium. The expression for Freundlich equation is given by

$$q_e = k_f C_e^{\frac{1}{n}} \qquad (4)$$

The linear form of Freundlich equation is given by the expression

$$\log \frac{x}{m} = \log k_f + \frac{1}{n} \log C_e \qquad (5)$$

Where, x is the amount of the dye adsorbed at equilibrium (mg), m is the weight of adsorbent used (mg) and C_e is the equilibrium concentration of the dye in solution (mg/L). K_f and n are the constants incorporating all factors affecting the adsorption process. Linear plot of $\log \frac{x}{m}$ Vs. $\log C_e$ show that the adsorption follows Freundlich isotherm. The linear plots of Ce/qe Vs Ce suggest the applicability of Langmuir isotherms Fig.4.5. The values of Q_m and b were determined from slope and intercepts of the plots and are presented in Table. 4.

The constant Q_o (mg/g) is a measure of maximum adsorption capacity of the adsorbent under the experimental conditions and b (L/mg) is a constant related to the energy of adsorption. The result indicates that the adsorption capacity of LIS carbon is moderate and does not vary much with temperature. The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless separation factor R_L. The values of R_L at various initial dye concentrations are given in Table. 5. The value of R_L indicates the shape of the isotherm to be unfavourable, linear, favourable or irreversible. R_L values for the present experimental data fall between 0 and 1, which is an indication of favourable adsorption of acid violet 4BS on the adsorbent. For the analysis of Freundlich isotherm, a linear graph of log q_e Vs log C_e was plotted in Fig. 4.6. The Freundlich constants n and k_f were determined from the slope and intercept of the plot respectively. The constant n indicates the bond energies between dye and the adsorbent, whereas k_f (mg/L) is related to bond strength. The values of Freundlich isotherm parameters were given in Table. 6. Results shows that the experimental data was better described by the Langmuir isotherm compared to the Freundlich isotherm. The graph plotted from the Langmuir model yielded a straight line with higher regression co-efficient value (0.912 to 0.964). In contrast, the Freundlich isotherm model was less precise, with lower R^2 value (0.749 to 0.892). The value of R^2 is regarded as a measure of the goodness of fit of experimental data on the isotherm models. Thus, the data of Acid Violet 4BS adsorption on LIS activated carbon may be concluded to perfectly fit the Langmuir isotherm model. This indicates that the adsorption of Acid Violet 4BS on LIS activated carbon takes place as monolayer adsorption on the adsorbent surface and homogeneous in adsorption affinity.

3.6. Effect of pH on dye removal

The effect of pH of the solution (pH from 2 to 10) on the adsorption of Acid Violet 4BS of concentration 40mg/L by Lagerstroemia Indica seed carbon of dosage 50mg was determined. The results were shown in figure 4.7. The pH of the solution was controlled by the addition of 0.1N HCl or 0.1N NaOH. The maximum uptake of Acid Violet 4BS was obtained at pH 2. However, when the pH of the solution was increased, the uptake of Acid Violet decreases gradually.

3.7. Effect of pH and initial dye concentration

Since, the maximum uptake of dye by the adsorbent was obtained at pH 2, the effect of different initial dye concentrations on the percentage of dye removal at a fixed adsorbent dosage of 50mg per 50ml of dye solution were studied at pH 2. It is evident that as the concentration of initial dye increases, the percentage of dye removal decreases for both pH of 7.35 (normal pH of dye solution) and pH of 2. However, the rate of decrease in the percentage of dye removal with increase in initial dye concentration was less at pH 2 when compared to pH 7.35. The maximum percentage of dye removal (86.67%) was obtained at an initial dye concentration of 10 mg/L and at pH 2 with adsorbent dosage of 50 mg per 50 ml of dye solution.

3.8. Effect of pH and adsorbent dosage

The effect of adsorbent dosage with a fixed initial dye concentration of 40 mg/L at pH 2 and the results were summarized in Table.7 From the results it is evident that the amount of dye removed (mg/g) decreases with increase in adsorbent dosage eventhough the percentage of dye removal increases. However, the amount of dye removed is considerably high at pH 2 rather than at pH 7.35. When the concentration of dye solution is 40 mg/L, the maximum amount of dye removal takes place with an adsorbent dosage of 25 mg per 50 ml of dye solution at a pH value of 2.

3.9. Thermodynamic parameters

The ΔS°, ΔH° and ΔG° values obtained at different temperatures for various initial dye concentrations were presented in Table.8. The negative values of ΔH° show the exothermic nature of adsorption and it governs the possibility of chemisorption rather than physical adsorption. In the case of physical adsorption, increase in temperature of the system increases the extent of dye adsorption. This rule out the possibility of physical adsorption. From the results it was evident that ΔG° has both positive and negative values depending upon the concentration of initial dye solution and temperature. The systems with negative values of ΔG° were favourable and spontaneous whereas those systems with positive values of ΔG° were unfavourable. The negative value of ΔS° indicates that the randomness at the adsorbent- solution interface decreases during the adsorption.

3.10. Scanning Electron Microscope

SEM micrographs (Fig.4.8 and Fig.4.9) of activated carbon particles showed cavities, pores and more rough surfaces on the carbon sample. Granular pores and cavities will increase the surface area of the adsorbent. SEM photograph of LIS shows that the surface is pitted and fragmented due to the carbonization with HCl acid and activation process. The surface area of the LIS will be enhanced by the presence of more porosity, which can hold more solute from solution during adsorption.

IV. FIGURES AND TABLES

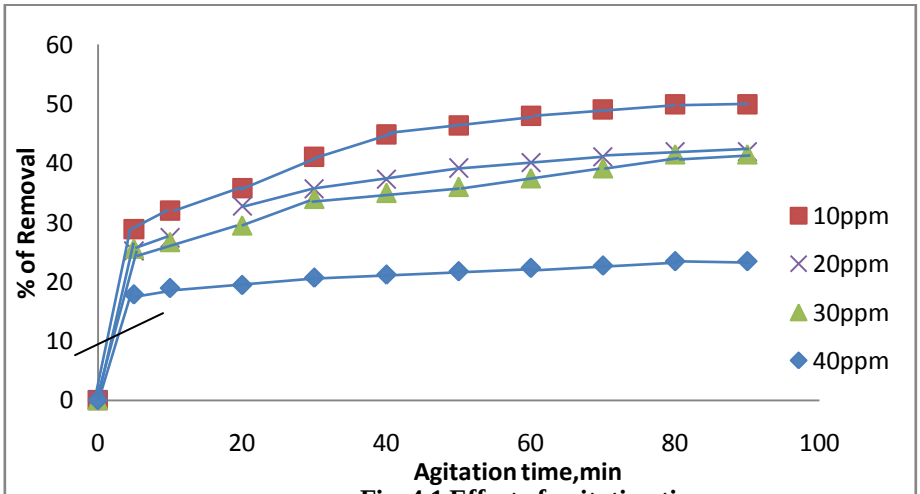

Fig. 4.1 Effect of agitation time

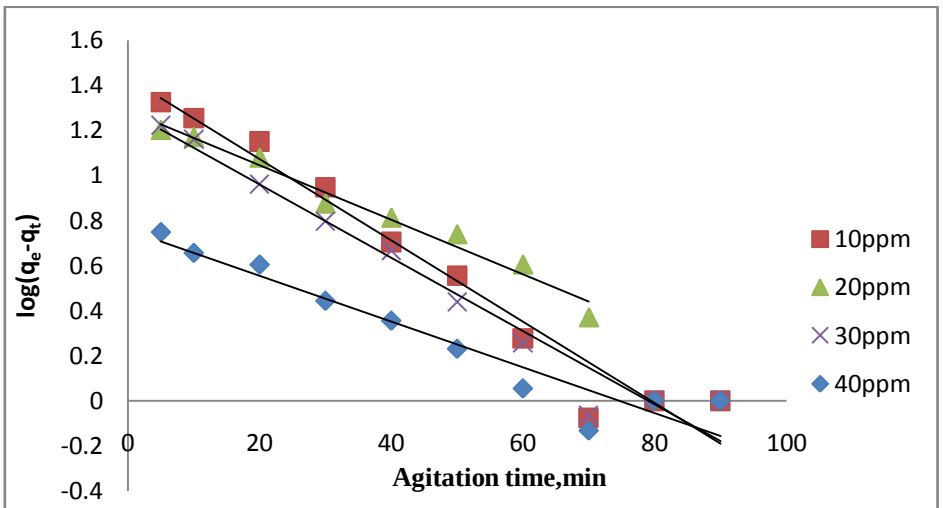

Fig. 4.2 Lagergren plots for Pseudo first order

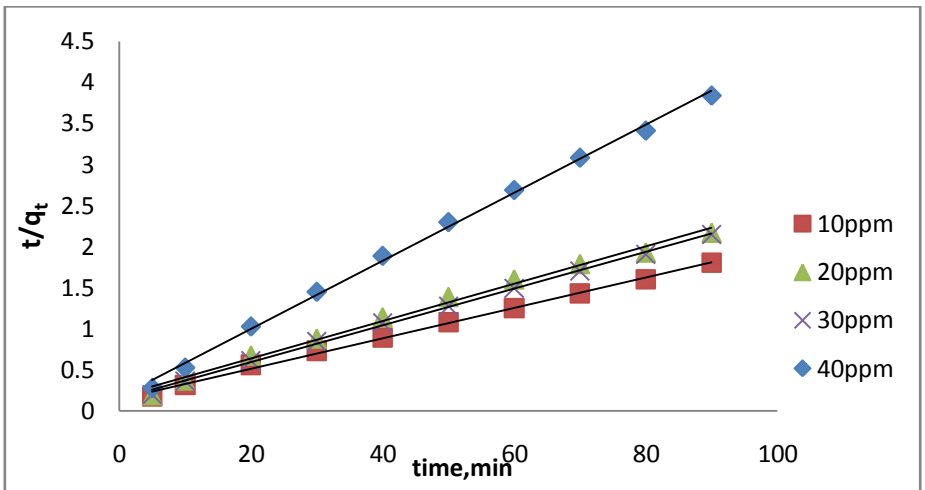

Fig. 4.3 Pseudo second order plot

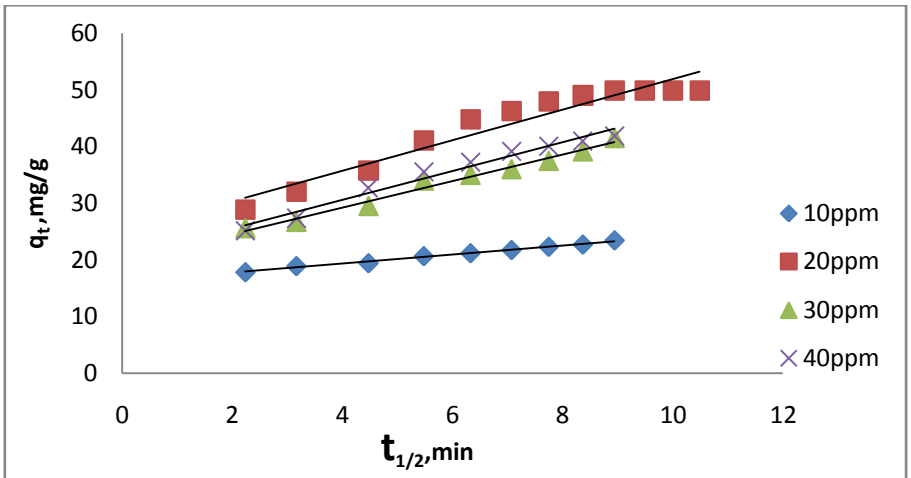

Fig . 4.4 Intra particle diffusion plot

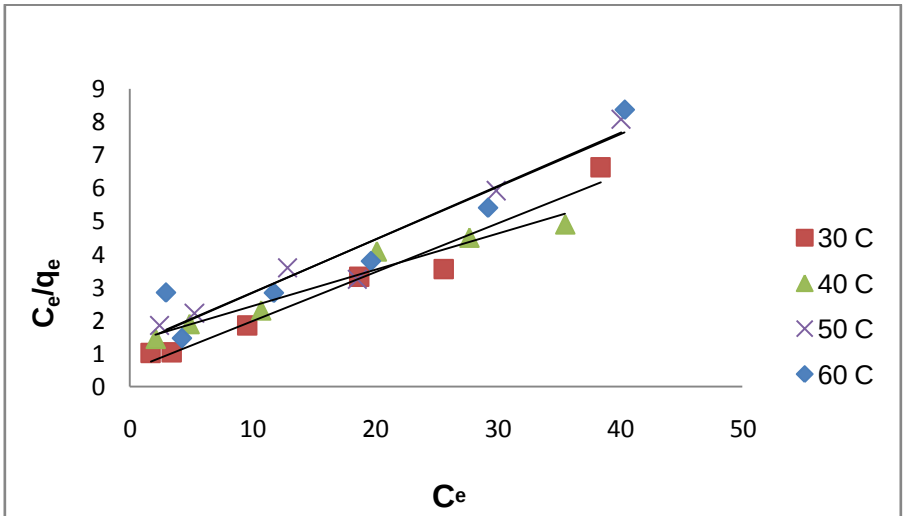

Fig. 4.5 Langmuir isotherm plot

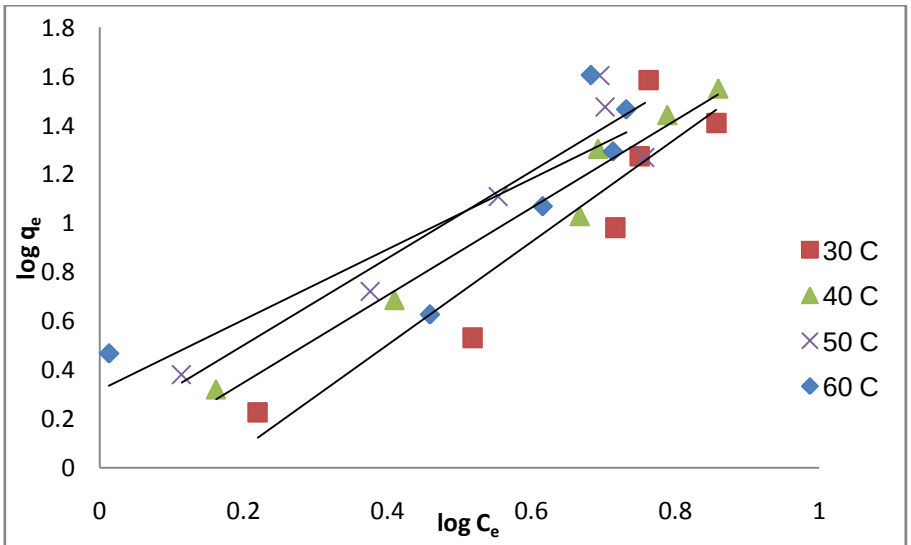

Fig. 4.6 Freundlich Isotherm plot

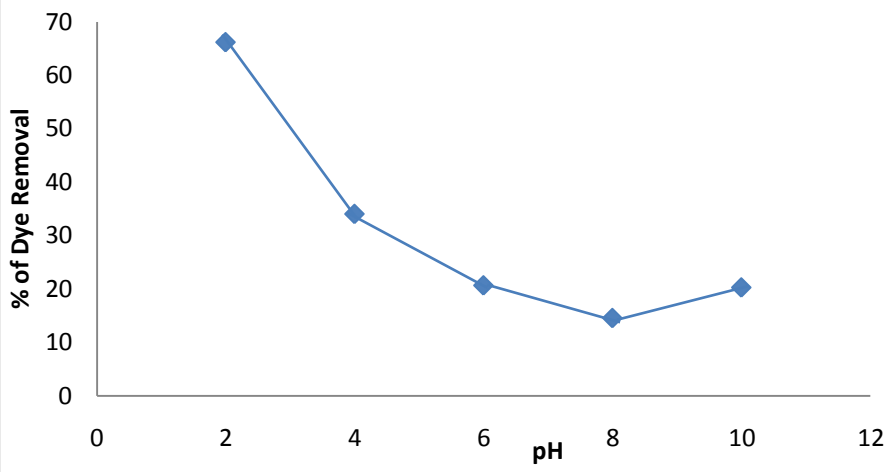

Fig. 4.7 Effect of pH

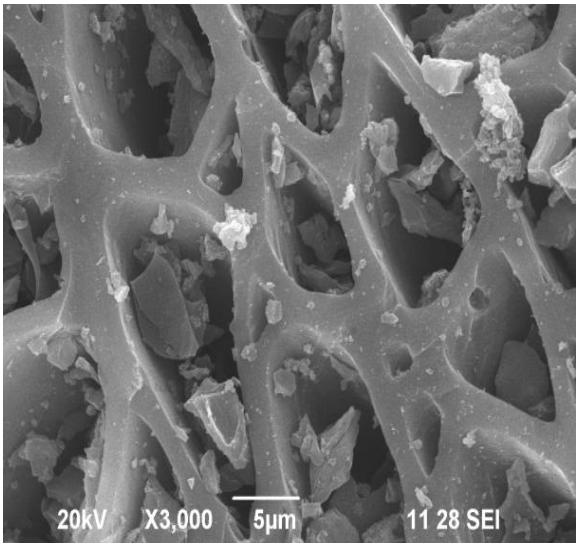

Fig. 4.8 SEM photograph of LIS (3000 X)

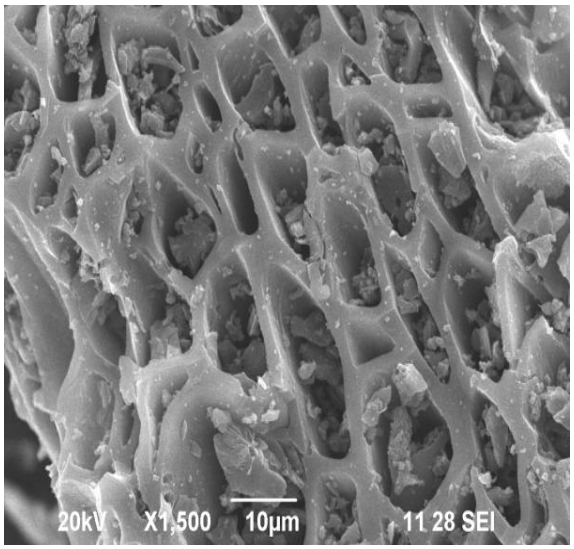

Fig. 4.9 SEM photograph of LIS (1500 X)

Table. 1
Physical and chemical properties of LIS used in the experiments

pH 1% solution	7.35
Moisture Content,(%)	2.18
Ash Content,(%)	0.29
Conductivity (ms/cm)	0.21
Surface area, m^2/g	289
Bulk density, gm/L	0.38
Specific gravity porosity	1.28
Iodine number, mg/g	399
Water – soluble matter, %	0.12
HCl soluble matter, 0.25N, %	1.31%
Particle size, µm	300
Yield	42%

Table. 2
Amount of dye removed (mg/g) at various initial dye concentration and adsorbent dosage

Initial dye concentration (mg/L)	Adsorbent dosage (mg)/50 ml			
	25	50	75	100
10	-	49.89	42.38	37.18
20	49.36	41.48	31.30	27.71
30	-	41.88	26.41	18.63
40	31.23	23.44	19.13	20.84

Table. 3
Pseudo first and pseudo second-order kinetic parameters for different initial dye concentration

Initial Dye Concentration (mg/L)	q_e, exp. (mg/L)	Pseudo first-order Kinetic Model			Pseudo second – order kinetic Model		
		q_e, cal. (mg/L)	k_1 (1/mm)	R^2	q_e, cal. (mg/L)	k_2 (g/mg.min.)	R^2
10	49.89	13.91	0.0414	0.958	55.5	2.32×10^{-3}	0.997
20	41.48	13.45	0.0276	0.975	45.45	2.69×10^{-3}	0.991
30	41.88	13.44	0.0368	0.961	45.45	3.36×10^{-3}	0.998
40	23.44	5.715	0.0230	0.916	24.30	1.27×10^{-2}	0.997

Table. 4
Langmuir isotherm parameters

Tem.p (°C)	Statistical Parameters / Constants		
	R^2	Q_o (mg/g)	b. (L/mg)
30	0.964	6.80	0.2911
40	0.956	9.17	0.0812
50	0.955	6.21	0.1323
60	0.912	6.28	0.1268

Table 5
R_L values at various initial dye concentrations

Initial Dye Concentration (mg/L)	R_L value			
	30°C	40°C	50°C	60°C
5	0.4073	0.7112	0.6018	0.6199
10	0.2557	0.5518	0.4305	0.4409
20	0.1465	0.3811	0.2742	0.2828
30	0.1027	0.2910	0.2012	0.2082
40	0.0790	0.2354	0.1589	0.1647
50	0.0642	0.1976	0.1313	0.1362

Table. 6
Freundlich isotherm parameters

Temp. (°C)	Statistical Parameters / Constants		
	R^2	N	K_f (mg/L)
30	0.857	0.4757	1.725
40	0.969	0.5602	1.529
50	0.892	0.5624	1.390
60	0.749	0.6930	1.075

Table. 7
Amount of dye removed (mg/g) at various adsorbent dosage at a particular pH

Adsorbent dosage (mg) per 50 ml of dye solution	Amount of dye removed (mg/g)	
	pH = 7.35	pH =2
25	31.23	129.04
50	23.44	66.17
75	19.13	52.97
100	20.84	46.21

Table. 8.
Thermodynamic Parameters

Initial dye concentration, mg/L	ΔS° J/mol/K	ΔH° KJ/mol	ΔG° (KJ/mol)		
			303K	313K	323K
5	-86.63	-27.99	-1.75	-0.875	-0.01
10	-80.95	-25.91	-1.39	-0.58	+0.23
20	-48.90	-14.87	-0.054	+0.435	+0.92
40	-48.23	-13.02	+1.593	+2.07	+2.558
50	-41.37	-9.885	+2.65	+3.063	+3.47

V. CONCLUSION

The kinetic studies shows that the adsorption of Acid Violet 4BS on *Lagerstroemia Indica* seed activated carbon is well-fitted to pseudo second-order kinetic model suggesting that the adsorption process was controlled by chemisorptions. The results of adsorption isotherm studies shows that the experimental data were better described by Langmuir isotherm compared to Freundlich isotherm suggesting monolayer adsorption of the dye on the adsorbent surface. When the pH of the solution was increased, the uptake of Acid Violet 4BS dye by the adsorbent decreases gradually. The maximum removal of Acid Violet 4BS by the adsorbent was obtained at pH 2. The maximum percentage of dye removal (86.67%) was obtained at an initial dye concentration of 10mg/L with adsorbent dosage of 50 mg per 50 ml of dye solution. The negative value of ΔH° shows that the adsorption of Acid Violet 4Bs dye on Lagerstroemia Indica seed activated carbon was exothermic in nature. From the present study it is obvious that the adsorption capacity of activated carbon prepared from *Lagerstroemia Indica* seed is comparable with that of other low cost waste activated carbon. The results obtained will be useful for the design of dyeing industry effluent treatment plants.

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