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## Kinetic And Thermodynamic Studies On The Adsorption Of Dyes Onto Low Cost Activated Carbon

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### ABSTRACT

Batch experiments were carried out for the sorption of Congo red, Malachite green; Rhodamine B and Rose Bengal dyes onto acid activated carbon. The operating variables studied were initial dye concentration, pH, temperature and contact time. Equilibrium data fitted to the Langmuir and Freundlich isotherm equations. From this adsorption efficiency, adsorption energy, adsorption capacity and intensity of adsorption were calculated. From the kinetic studies the rate constant values for the adsorption process was calculated. Thermodynamic parameters like  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  for the adsorption were also calculated. The mechanism of adsorption of the dyes onto the carbon have confirmed by FT-IR, XRD and SEM images.

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### KEYWORDS

Dyes;  
 Activated carbon;  
 Adsorption;  
 Isotherms.

### INTRODUCTION

The discharge of highly coloured effluents into natural water bodies is not only aesthetically displeasing, but it also impedes light penetration, thus upsetting biological processes within a stream. In addition, many dyes are toxic to some organisms causing direct destruction of aquatic communities. Some dyes can cause allergic dermatitis, skin irritation, cancer and mutation in man. Recent estimates indicate that, approximately, 12% of synthetic textile dyes used each year lost during manufacture and processing operation and 20% of these dyes enter the

environment through effluents that result from the treatment of residual industrial waters. Among the various classes of dyes, basic dyes have found to be the brightest class of soluble dyes used by the textile industry as their tinctorial value is very high<sup>[1]</sup>.

Wastewaters from dyeing industries released into nearby land or rivers without any treatment because the conventional treatment methods are not cost effective in the Indian context. On the other hand, low cost technologies never allow a wishful colour removal and it has certain disadvantages. Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely em-

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ployed to treat wastewater containing different classes of dyes, recognizing the economic drawback of commercial activated carbon. Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, saw dust buffing dust of leather industry, coir pith, crude oil residue tropical grass, olive stone and almond shells, pine bark, wool waste, coconut shell etc., as carbonaceous precursors for the removal of dyes from water and wastewater<sup>[2-6]</sup>. The present study is undertaken to evaluate the efficiency of a carbon adsorbent prepared from acid activated *Sesbania grandiflora*(Linn)Poir. carbon for removal of dyes from aqueous solution. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer processes is essential. In this paper, we report the applicability of kinetic and mass-transfer models for the adsorption of Congo red, Malachite green, Rhodamine B and Rose Bengal onto activated carbon. These four dyes were chosen so as to have different classes of dyes i.e. Congo red, Malachite green, Rhodamine B and Rose Bengal belong to azo, triarylmethane, rhodamine and fluorone classes respectively. Further Congo red and Rose Bengal are acid dyes whereas Malachite green and Rhodamine B are basic in nature.

### MATERIALS AND METHODS

#### Materials

Dried leaves of *Sesbania grandiflora*(Linn.)Poir. were carbonized with concentrated sulphuric acid in ratio of 1:1(w/v). The carbonization and activation has completed by heating for twelve hours in a furnace at 400°C. The resulting carbon washed with distilled water until a constant pH of the slurry reached. Then the carbon has dried for four hours at 100°C in a hot air oven. The dried material was ground well to a fine powder and sieved. Characterization of the adsorbent was done by employing conventional analytical/chemical methods. The zero point charge of the adsorbent was estimated by reported method<sup>[7]</sup>.

All Chemicals used were of high purity, commercially available Analar grade. Stock solutions of

the dyes were prepared using doubly distilled water.

#### Methods

Congo red(CR, C.I. 22120), Malachite green(MG, C.I. 42000), Rhodamine B(RDB, C.I. 45170) and Rose Bengal(RB, C.I. 45440) dyes were made to a known concentration. From this 50 ml of 10-60mg/L dye solutions have taken and added with the known quantity of activated carbon adsorbent. Then these were agitated at 30<sup>o</sup>, 40<sup>o</sup>, 50<sup>o</sup>, and 60<sup>o</sup>C in a defined time intervals, samples are withdrawn from the shaker and filtered. Then it is analyzed in a Shimadzu UV-Visible double beam spectrophotometer.

Desorption studies were carried out using the spent carbon. The carbon loaded with dyes separated and gently washed with distilled water to remove any unadsorbed dyes. The dye-laden carbons were agitated with 50ml each of water, sulphuric acid, hydrochloric acid, and nitric acid and sodium chloride solutions(all 0.2 M) separately for 30minutes and analyzed. The XRD patterns of the adsorbents before and after adsorption were recorded at the Regional Research Laboratory, Thiruvananthapuram, S.India. The SEM images were recorded at Madurai Kamaraj University, Madurai, S.India.

### RESULTS AND DISCUSSIONS

#### Sorbent characterization

The physicochemical characteristics of the acid activated *Sesbania grandiflora* (Linn) Poir carbon (SGC) used in the study are given below.

Adsorbent	Particle size (mm)	Density (g/cc)	Moisture Content (%)	Loss on ignition	Acid insoluble matter	Water soluble matter	pH	pH <sub>ZPC</sub>
SGC	0.14	0.5293	1.20	85.2	5.0	0.34	7.0	6.5

#### Effect of initial dye concentration

The effect of initial concentration of the sorbent was studied and the results of the equilibrium studies were collected in TABLE 1. The results reveal that, percent adsorption decreased with increase in initial dye concentration, but the actual amount of dyes adsorbed per unit mass of carbon increased with increase in dyes concentration. It means that the adsorption is highly dependent on initial con-

**TABLE 1 : Equilibrium parameters for the adsorption of dyes onto activated carbon**

[D] <sub>0</sub>	C <sub>e</sub> (mg L <sup>-1</sup> )				Q <sub>e</sub> (mg g <sup>-1</sup> )			Dye removed(%)				
	30 <sup>o</sup>	40 <sup>o</sup>	50 <sup>o</sup>	60 <sup>o</sup>	30 <sup>o</sup>	40 <sup>o</sup>	50 <sup>o</sup>	60 <sup>o</sup>	30 <sup>o</sup>	40 <sup>o</sup>	50 <sup>o</sup>	60 <sup>o</sup> C
<b>Congo red adsorption</b>												
10	2.74	2.50	2.35	2.19	1.45	1.50	1.53	1.52	72.6	75.0	76.5	78.1
20	5.79	5.47	5.16	4.85	2.84	2.91	2.97	3.03	71.1	72.7	74.2	75.8
30	8.84	8.41	8.05	7.62	4.23	4.32	4.39	4.48	70.5	71.9	73.2	74.6
40	12.67	12.12	11.53	10.95	5.47	5.58	5.69	5.81	68.3	69.7	71.2	72.6
50	16.65	15.87	15.07	14.23	6.67	6.83	6.99	7.15	66.7	68.3	69.9	71.5
60	21.04	20.33	19.35	18.61	7.74	7.93	8.13	8.28	64.9	66.1	67.8	68.9
<b>Malachite green adsorption</b>												
10	1.20	1.17	1.14	1.12	1.76	1.76	1.77	1.78	88.0	88.3	88.6	88.8
20	2.76	2.66	2.53	2.49	3.45	3.47	3.49	3.50	86.2	86.7	87.4	87.6
30	4.60	4.47	4.35	4.20	5.08	5.11	5.13	5.16	84.7	85.1	85.5	86.0
40	6.68	6.50	6.33	6.15	6.66	6.70	6.73	6.77	83.3	83.7	84.2	84.6
50	8.89	8.67	8.44	8.21	8.22	8.27	8.31	8.36	82.2	82.7	83.1	83.6
60	11.49	11.21	10.94	10.67	9.70	9.76	9.84	9.87	80.9	81.3	81.8	82.2
<b>Rhodamine B adsorption</b>												
10	3.24	3.03	2.86	2.25	0.68	0.69	0.72	0.78	67.6	69.7	71.4	77.5
20	6.60	6.44	6.28	5.14	1.34	1.36	1.37	1.49	67.0	67.8	68.6	74.3
30	12.52	11.52	10.05	8.72	1.75	1.85	1.99	2.13	58.3	61.6	66.5	70.9
40	17.18	15.56	14.25	12.71	2.28	2.44	2.58	2.73	57.0	61.1	64.4	68.2
50	21.51	20.19	19.49	16.76	2.85	2.98	3.05	3.32	56.9	59.6	61.0	66.5
60	25.93	24.44	23.50	21.14	3.41	3.56	3.65	3.89	56.8	59.3	60.8	64.8
<b>Rose Bengal adsorption</b>												
10	4.97	4.72	4.35	4.00	0.25	0.26	0.28	0.30	50.3	52.8	56.5	60.0
20	10.52	9.56	8.81	8.07	0.47	0.52	0.56	0.60	47.4	52.2	55.9	59.7
30	16.26	15.33	14.32	13.59	0.69	0.77	0.78	0.82	45.8	48.9	52.3	54.7
40	22.78	21.23	19.62	18.65	0.86	0.94	1.02	1.07	43.0	46.9	50.9	53.4
50	30.66	28.31	27.28	25.92	0.97	1.08	1.14	1.20	38.7	43.4	45.4	48.2
60	39.11	36.71	35.60	34.54	1.05	1.16	1.22	1.27	34.8	38.8	40.7	42.4

centration of dye. It is because of the fact that at lower concentration, the ratio of the initial number of dye molecules 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 concentration<sup>[8]</sup>.

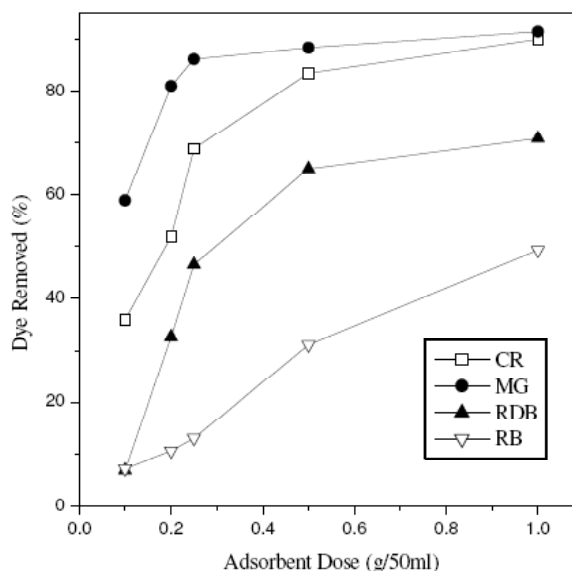
**Effect of dose of the adsorbent**

The adsorption of the dyes on the carbon was studied by varying the dose of the carbon (100-1000mg/50ml) at a fixed dye concentration. The percent adsorption increased with increase in the carbon dose (Figure 1). This has attributed to increased carbon surface area and availability of more adsorption sites<sup>[9]</sup>.

**Adsorption isotherm**

The experimental data were analyzed according to the linear form of the Langmuir<sup>[10]</sup> and

Freundlich<sup>[11]</sup> isotherms. The Langmuir isotherm is represented by the following equation.



**Figure : 1 Effect of adsorbent dose on the removal of dyes [Dye]=20mg/L; pH=7; Temp=30°C; Time=1Hr**

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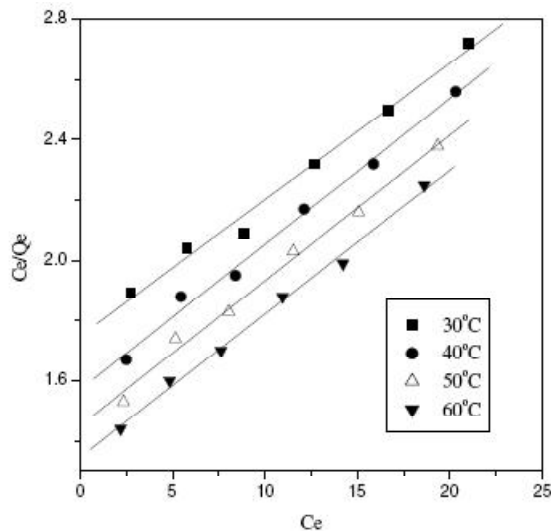


Figure 2 : Linear langmuir plot's for the adsorption of congo red onto activated carbon

TABLE 2 : Langmuir isotherm results

Dye	Temp. °C	Statistical parameters/constants			
		r	sd	Q <sup>0</sup>	b
Congo red	30	0.995	0.03	22.22	0.026
	40	0.996	0.03	20.70	0.031
	50	0.996	0.03	20.75	0.033
	60	0.997	0.02	20.96	0.035
Malachite green	30	0.991	0.03	21.10	0.072
	40	0.992	0.02	21.19	0.074
	50	0.992	0.03	21.01	0.078
	60	0.994	0.02	21.32	0.078
Rhodamine B	30	0.901	0.66	7.09	0.031
	40	0.940	0.41	8.13	0.029
	50	0.987	0.17	8.06	0.033
	60	0.987	0.17	7.46	0.048
Rose Bengal	30	0.986	1.20	1.99	0.030
	40	0.966	1.50	2.29	0.030
	50	0.977	1.20	2.26	0.036
	60	0.982	1.14	2.18	0.045

$$C_e/Q_e = 1/Q_0 b + C_e/Q_0$$

where  $C_e$  is the equilibrium concentration (mg/L),  $Q_e$  is the amount adsorbed at equilibrium (mg/g) and  $Q_0$  and  $b$  are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of  $C_e/Q_e$  versus  $C_e$  suggest the applicability of the Langmuir isotherms and a representative plot is given in figure 2. Values of  $Q_0$  and  $b$  were determined from slope and intercepts of the plots and are presented in TABLE 2. Linear Langmuir plots suggest that the adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface. To confirm the

TABLE 3 : Equilibrium parameter,  $R_L$

[Dye](mgL <sup>-1</sup> )	Temperature (°C)			
	30	40	50	60
<b>Congo red adsorption</b>				
10	0.794	0.763	0.752	0.741
20	0.658	0.617	0.602	0.588
30	0.562	0.518	0.503	0.488
40	0.490	0.446	0.431	0.417
50	0.435	0.392	0.377	0.364
60	0.391	0.349	0.336	0.322
<b>Malachite green adsorption</b>				
10	0.581	0.575	0.562	0.562
20	0.410	0.403	0.391	0.391
30	0.316	0.310	0.299	0.299
40	0.258	0.252	0.243	0.243
50	0.217	0.213	0.204	0.204
60	0.188	0.184	0.176	0.176
<b>Rhodamine B adsorption</b>				
10	0.763	0.775	0.752	0.676
20	0.617	0.633	0.602	0.510
30	0.518	0.535	0.503	0.410
40	0.446	0.463	0.431	0.342
50	0.406	0.408	0.377	0.294
60	0.350	0.365	0.336	0.258
<b>Rose Bengal adsorption</b>				
10	0.769	0.769	0.735	0.690
20	0.625	0.625	0.581	0.526
30	0.526	0.526	0.481	0.426
40	0.454	0.454	0.410	0.357
50	0.400	0.400	0.357	0.308
60	0.357	0.357	0.316	0.270

favorability of the adsorption process, the separation factor ( $R_L$ ) was calculated and presented in TABLE 3. The values were found to be between 0 and 1 and confirm that the ongoing adsorption process is favourable<sup>[12]</sup>. Further the results suggest that the adsorption becomes more favourable at high temperatures and high dye concentrations.

The Freundlich equation has also employed for the adsorption of the dyes on the adsorbent. The Freundlich isotherm is represented as,

$$\log Q_e = \log K + 1/n \log C_e$$

where  $Q_e$  and  $C_e$  has usual meanings and  $K$  and  $n$  are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of  $\log Q_e$  versus  $\log C_e$  shows that the adsorption of the dyes follows the Freundlich isotherm and a representative plot is given in figure 3. The statistical results and constants are collected in TABLE 4. The results indicates that the order of adsorption capacity as  $MG > CR > RDB > RB$ , the

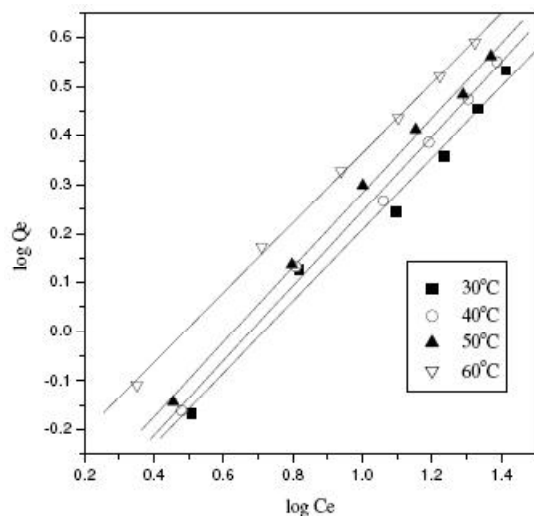


Figure 3 : Freundlich isotherms for the adsorption of Rhodamine B onto activated carbon

trend shows the increase of negative charge on the surface that enhances the electrostatic force like van der Waal's between the carbon surface and dye ion, which increases the adsorption of MG, CR compared to RB. The higher molecular weight, large size and radii of the RB and RDB have shown the limited possibility of the adsorption of these dyes onto adsorbent<sup>[13]</sup>. The values of *n* are greater than one indicating the adsorption is favourable<sup>[14]</sup>.

**Effect of temperature**

Thermodynamic parameters such as change in free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) were determined from the slope and intercept of van't Hoff plots as described earlier<sup>[15]</sup> and are collected in TABLE 5. The positive values of  $\Delta H^0$  show the endothermic nature of adsorption and the very low magnitude of enthalpy change depicts that the dyes are physisorbed onto the adsorbent<sup>[16]</sup>. The negative values of  $\Delta G^0$  indicates that all the four dye adsorption were spontaneous. The positive values of  $\Delta S^0$  show the increased disorder and randomness at the solid-solution interface. This may be due to the fact that, the adsorbed water molecules, which have displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system<sup>[17]</sup>.

**Kinetics of adsorption**

TABLE 4 : Freundlich isotherm results

Dye	Temp. °C	Statistical parameters/constants			
		r	sd	K	n
Congo red	30	0.998	0.02	0.65	1.21
	40	0.998	0.02	0.74	1.24
	50	0.997	0.02	0.75	1.22
	60	0.998	0.02	0.84	1.25
Malachite green	30	0.999	0.01	1.57	1.36
	40	0.999	0.01	1.61	1.32
	50	0.999	0.01	1.66	1.32
	60	0.999	0.01	1.69	1.32
Rhodamine B	30	0.992	0.03	0.30	1.37
	40	0.997	0.02	0.27	1.31
	50	0.999	0.01	0.33	1.31
	60	0.999	0.01	0.45	1.40
Rose Bengal	30	0.989	0.04	0.09	1.40
	40	0.985	0.05	0.09	1.35
	50	0.983	0.05	0.11	1.41
	60	0.981	0.05	0.13	1.47

TABLE 5 : Equilibrium constant and thermodynamic parameters for the adsorption of dyes onto activated carbon

[Dye] <sub>0</sub>	K <sub>n</sub>		-ΔG <sup>0</sup>				ΔH <sup>0</sup>	ΔS <sup>0</sup>		
	30 <sup>o</sup>	40 <sup>o</sup>	50 <sup>o</sup>	60 <sup>o</sup>	30 <sup>o</sup>	40 <sup>o</sup>			50 <sup>o</sup>	60 <sup>o</sup> C
<b>Congo Red adsorption</b>										
10	2.65	3.00	3.26	3.57	2.46	2.78	2.98	3.21	8.21	35.3
20	2.45	2.66	2.88	3.12	2.26	2.46	2.66	2.87	6.75	29.7
30	2.39	2.57	2.73	2.94	2.20	2.46	2.69	2.98	5.72	26.1
40	2.16	2.30	2.47	2.65	1.94	2.17	2.43	2.70	5.74	25.3
50	2.01	2.15	2.32	2.51	1.76	1.99	2.26	2.55	6.22	26.3
60	1.85	1.95	2.10	2.22	1.55	1.74	1.99	2.21	5.21	22.3
<b>Malachite Green adsorption</b>										
10	7.33	7.55	7.77	7.93	5.01	5.26	5.51	5.73	2.22	23.9
20	6.25	6.52	6.91	7.03	4.62	4.88	5.19	5.40	3.46	26.7
30	5.52	5.71	5.90	6.14	4.30	4.53	4.77	5.02	2.95	23.9
40	4.98	5.15	5.31	5.50	4.04	4.27	4.48	4.72	2.75	22.4
50	4.62	4.77	4.92	5.09	3.86	4.06	4.28	4.51	2.69	21.6
60	4.22	4.35	4.48	4.62	3.63	3.83	4.03	4.24	2.52	20.3
<b>Rhodamine B adsorption</b>										
10	2.09	2.30	2.50	3.44	1.86	2.17	2.46	3.42	13.1	49.0
20	2.03	2.11	2.18	2.89	1.78	1.94	2.09	2.94	9.03	35.3
30	1.40	1.60	1.99	2.44	0.85	1.22	1.85	2.47	15.8	54.6
40	1.33	1.57	1.81	2.15	0.72	1.17	1.59	2.12	13.3	46.1
50	1.32	1.48	1.57	1.98	0.70	1.02	1.21	1.90	10.6	37.2
60	1.31	1.45	1.55	1.84	0.68	0.97	1.18	1.69	9.07	32.1
<b>Rose Bengal adsorption</b>										
10	1.01	1.12	1.30	1.50	0.03	0.29	0.70	1.12	11.2	36.8
20	0.90	1.09	1.27	1.48	-0.27	0.22	0.64	1.09	13.8	44.8
30	0.85	0.96	1.09	1.21	-0.41	-0.11	0.23	0.53	9.96	31.5
40	0.75	0.88	1.04	1.14	-0.72	-0.33	0.11	0.36	15.4	48.3
50	0.63	0.77	0.83	0.93	-1.16	-0.68	-0.50	-0.20	10.5	30.9
60	0.53	0.63	0.68	0.74	-1.60	-1.20	-1.04	-0.83	9.10	24.9

ΔG<sup>0</sup>kJ mol<sup>-1</sup>; ΔH<sup>0</sup>kJ mol<sup>-1</sup>; ΔS<sup>0</sup>J K<sup>-1</sup> mol<sup>-1</sup>

Kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of the dye removal has been carried out to understand the behaviour of this low cost carbon adsorbent. The adsorption of



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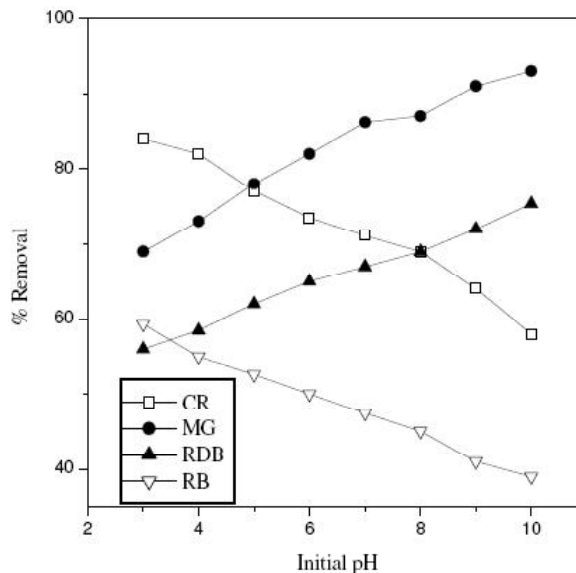
**TABLE 6 :** Rate constants for the adsorption of dyes ( $10^3 k_{ad}, \text{min}^{-1}$ ) and rate constants for the forward ( $10^3 k_1, \text{min}^{-1}$ ) and reverse ( $10^3 k_2, \text{min}^{-1}$ ) processes

[Dye] <sub>0</sub>	Temperature (°C)											
	$k_{ad}$				30		40		50		60	
	30°	40°	50°	60°	$k_1$	$k_2$	$k_1$	$k_2$	$k_1$	$k_2$	$k_1$	$k_2$
<b>Congo Red adsorption</b>												
10	5.33	5.80	6.15	6.62	3.87	1.46	4.35	1.46	4.71	1.44	5.17	1.45
20	5.07	5.33	6.64	5.97	3.60	1.47	3.88	1.45	4.19	1.45	4.53	1.44
30	4.62	5.22	5.44	5.70	3.97	1.65	3.76	1.46	3.98	1.46	4.25	1.45
40	3.55	4.05	3.83	4.45	2.42	1.13	2.82	1.23	2.73	1.10	3.24	1.11
50	3.66	3.67	4.10	4.17	2.44	1.22	2.51	1.16	2.86	1.24	2.99	1.18
60	3.58	3.60	3.78	3.86	2.31	1.27	2.38	1.22	2.56	1.22	2.66	1.20
<b>Malachite Green adsorption</b>												
10	5.53	5.85	5.97	6.69	5.09	0.44	5.16	0.69	5.29	0.68	5.94	0.75
20	4.35	5.02	4.73	5.53	3.75	0.60	4.33	0.69	4.12	0.61	4.84	0.69
30	3.09	4.67	4.91	4.96	2.61	0.48	3.97	0.70	4.20	0.71	4.27	0.69
40	3.63	4.05	4.16	3.93	3.13	0.50	3.39	0.66	3.50	0.66	3.33	0.60
50	3.27	3.94	4.23	4.11	2.69	0.58	3.26	0.68	3.52	0.71	3.43	0.68
60	4.15	4.29	4.54	4.83	3.46	0.69	3.49	0.80	3.71	0.83	3.97	0.86
<b>Rhodamine B adsorption</b>												
10	2.21	2.31	2.33	3.19	1.49	0.72	1.60	0.71	1.67	0.66	2.47	0.72
20	1.45	1.43	1.49	1.88	0.97	0.48	0.97	0.46	1.02	0.47	1.40	0.48
30	0.98	1.13	1.25	1.41	0.57	0.41	0.70	0.43	0.83	0.42	1.00	0.41
40	1.55	1.21	1.49	1.83	0.89	0.66	0.74	0.47	0.96	0.53	1.25	0.58
50	1.44	1.59	1.63	1.53	0.82	0.62	0.97	0.62	1.00	0.63	1.02	0.51
60	1.09	2.64	2.63	2.98	0.65	0.49	1.56	1.08	1.60	1.03	1.93	1.05
<b>Rose Bengal adsorption</b>												
10	5.80	6.05	6.52	7.48	2.93	2.87	3.20	2.85	3.69	2.83	4.48	3.00
20	4.44	4.85	5.07	5.73	2.10	2.33	2.52	2.33	2.84	2.23	3.42	2.31
30	5.45	5.65	5.85	8.41	2.50	2.95	2.76	2.89	3.04	2.81	4.60	3.81
40	5.02	5.44	5.77	6.19	2.16	2.86	2.55	2.89	2.93	2.84	3.30	2.89
50	4.76	5.13	5.38	5.75	1.92	3.04	2.23	2.90	2.44	2.94	2.77	2.98
60	4.61	4.75	4.91	4.66	1.60	3.01	1.84	2.91	1.99	2.92	1.98	2.68

dyes from an aqueous solution follows reversible first order kinetics, when a single species considered on a heterogeneous surface. The heterogeneous equilibrium between the dyes solution and the activated carbon have expressed as:



Where  $k_1$  is the forward rate constant and  $k_2$  is the backward rate constant. A represents dyes remaining in the aqueous solution and B represents dyes adsorbed on the surface of activated carbon. The rate constants for the adsorption of dyes onto the activated carbon were calculated as reported earlier and are furnished in TABLE 6. It is evident from the results that the forward rate constant is much higher than the backward rate constant suggesting that the rate of adsorption is clearly dominant. The rate constant for adsorption,  $k_{ad}$ , increases with increase of temperature suggesting endothermic nature of the adsorption process. Further, it decreases with increase of initial concentration of the dye. In cases of strict surface adsorption a variation of rate



**Figure 4 :** Effect of pH on the removal of dyes by activated carbon

should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial dye concentration and rate of reaction will not be linear. It shows that pore diffusion limits the overall rate of dye adsorption<sup>[18]</sup>.

### Effect of pH

The effect of initial solution pH on the amount of dyes adsorbed(%) at equilibrium conditions is shown in figure 4. The results indicate that the amount of Congo red and Rose Bengal decreases with increase in pH while that of Malachite green and Rhodamine B increases with increase in pH of the medium. This behavior can be explained on the basis of zero point charge of the adsorbent ( $pH_{ZPC}=6.5$ ). At lower pH below this point, the  $H^+$  ions compete effectively with cationic dyes viz. Malachite green and Rhodamine B causing a decrease in percentage of dye removal. At a higher pH above this zero point charge, the surface of the adsorbent gets negatively charged, which enhances the adsorption of positively charged dye cations through electrostatic force of attraction. As expected the anionic dyes Congo red and Rose Bengal show opposite behavior<sup>[19]</sup>.

### Desorption studies

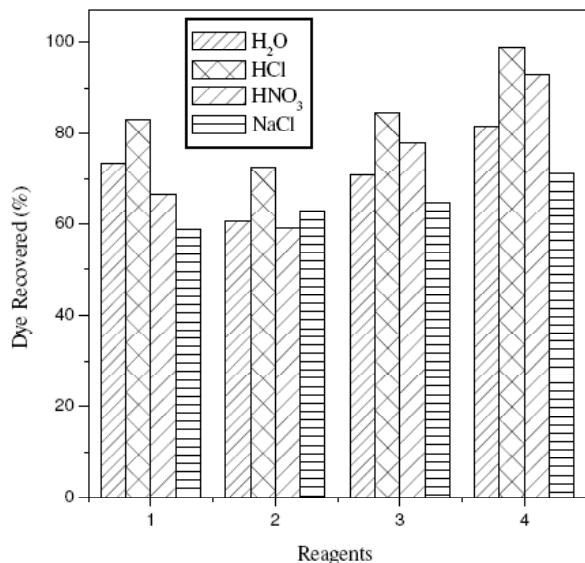


Figure 5 : Regeneration pattern of the spent carbon (1, CR ; 2, MG ; 3, RDB ; 4, RB)

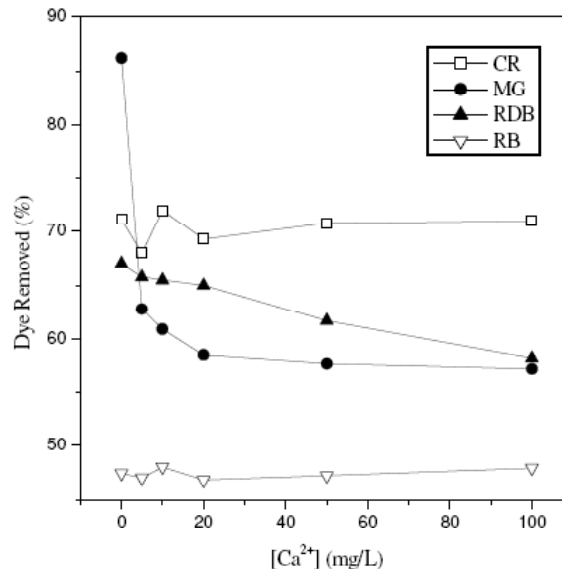


Figure 7 : Effect of added calcium ion on the adsorption of dyes

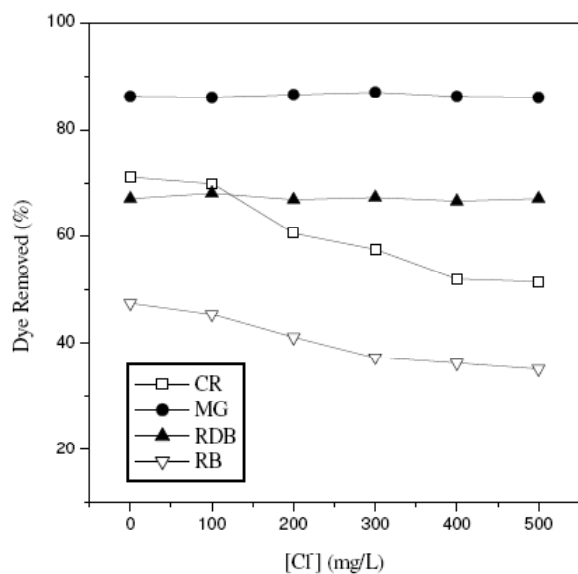


Figure 6 : Effect of added chloride ion on the adsorption of dyes

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent. If the adsorbed dyes can be desorbed using water, then the attachment of the dye of the adsorbent is by weak bonds. If acid or alkaline water desorb the dye, then the adsorption is by ion exchange. If organic acids, like acetic acid can desorb the dye, then the dye has held by the adsorbent through chemisorption<sup>[20]</sup>. The effect of various reagents used for desorption studies is shown in figure 5. The results indicate that water can able to desorb over 60% of

the adsorbed dye molecules and hence the adsorption of the dyes onto the activated carbon, in the present study, is a physical process. Hydrochloric acid was found to be a better reagent for desorption, because we could get more than 90% removal of adsorbed dye.

**Effect of other ions**

The effect of other ions like Ca<sup>2+</sup> and Cl<sup>-</sup> on the adsorption process was studied at different concentrations. The ions added to 20mg/L of dye solutions and the contents were agitated for 60 min at 30°C. The results(Figure 6-7) reveal that addition of chloride ions decreases the adsorption of anionic dyes namely CR and RB while calcium ions decreases the adsorption of cationic dyes, MG and RDB. This may be due to the fact that with increase in the concentration of these ions the interference at available surface sites of the sorbent through competitive adsorption increases and hence the percentage of dye adsorption decreases. The interference was more in the presence of Ca<sup>2+</sup> compared with Cl<sup>-</sup> ion. This is so because ions with smaller hydrated radii decrease the swelling pressure with in the sorbent and increase the affinity of the sorbent for such ions<sup>[21]</sup>.

**Spectral studies**

The FT-IR spectra of the activated carbon before and after adsorption of dyes have been recorded

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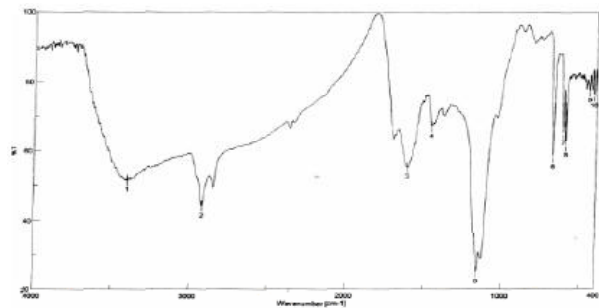


Figure 8a : FT-IR spectrum of the adsorbent before adsorption

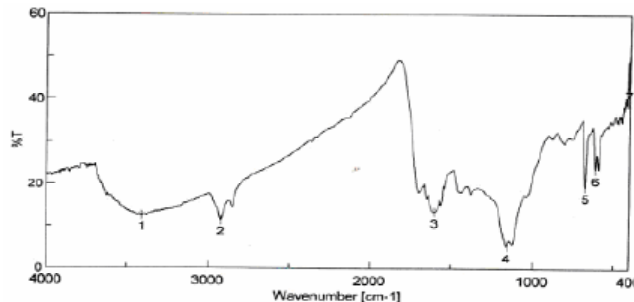


Figure 8b : FT-IR spectrum of the adsorbent after adsorption of Congo red

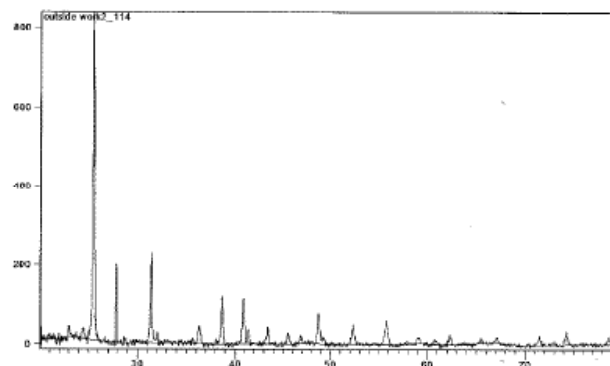
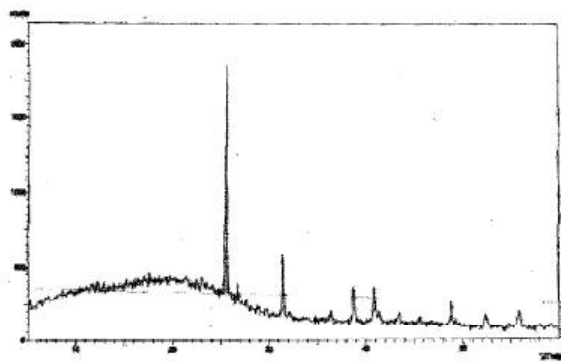


Figure 9 : XRD pattern of the adsorbent before adsorption(above) and after adsorption of Rhodamine B(below)

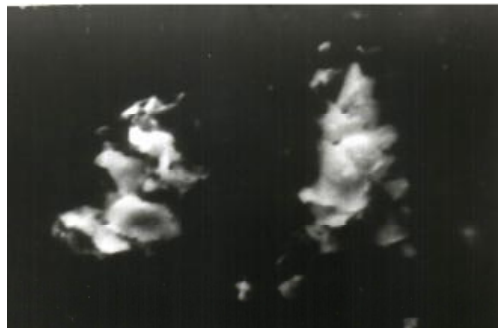
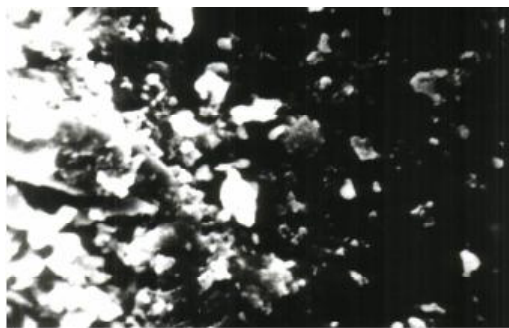


Figure 10 : SEM images of the adsorbent before adsorption (above) and after adsorption of Malachite green (below)

and a representative spectrum is shown in figure 8. It could be seen that the slight reduction of stretching vibration adsorption bands but not a change in peak positions. This clearly indicates the adsorption of dyes on the adsorbent by physical forces not by chemical combination. A representative XRD pattern of the activated carbon and dye-loaded carbon is shown in figure 9. The intense main peak shows the presence of highly organized crystalline structure of raw activated carbon<sup>[20]</sup>, after the adsorption of dyes, the intensity of the highly organized peaks

are slightly diminished. This has attributed to the adsorption of dye on the upper layer of the crystalline structure of the carbon surface by means of physisorption. The SEM images of raw activated carbon and dye-adsorbed activated carbon have been recorded and a representative image is given in figure 10. The bright spots, shows the presence of tiny holes on the crystalline structure of raw activated carbon, after treatment with dyes the bright spots became black shows the adsorption of the dyes on the surface of the carbon<sup>[22-23]</sup>.



**CONCLUSIONS**

The experimental data correlated reasonably well by the Langmuir and Freundlich adsorption isotherms and the isotherm parameters were calculated. The amount of dyes adsorbed increased with increase in temperature. The dimensionless separation factor ( $R_L$ ) showed that the activated carbon can be used for the removal of dyes from aqueous solution. The values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  show that the carbon employed has a considerable potential as an adsorbent for the removal of dyes. The results of spectral studies in consonance with thermodynamic parameters suggest that the adsorption of dyes over the activated carbon is a physical process.

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