

Full Length Research Paper

# Correlation investigation on the adsorption kinetics and thermodynamics of dyes onto acid triggered low cost carbon

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Batch experiments are carried out for the sorption of Congo red, Malachite green and Rhodamine B dyes onto acid activated carbon. The operating variables studied are initial dye concentration, pH, temperature and contact time. The equilibrium data are fitted to the Langmuir and Freundlich isotherm equations. From these the adsorption efficiency, adsorption energy, adsorption capacity, intensity of adsorption and dimensionless separation factor are calculated. The rate constant value for the adsorption process is calculated. The temperature thermodynamic parameters like  $G^\circ$ ,  $H^\circ$ , and  $S^\circ$  are calculated from the effect of temperature. The mechanism of dye adsorption for that dye onto carbon is investigated by using the experimental results.

**Key words:** Pandanus carbon, Congo red, Malachite green, Rhodamine B dyes, Adsorption isotherms- Langmuir and Freundlich isotherms, Adsorption energy, Adsorption efficiency, Kinetic studies, Thermodynamic parameters, pH effect, Effect of other ions, Regeneration pattern.

## 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 are 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 (Weber and Stickney, 1993). Among the various classes of dyes, basic dyes are found to be the brightest class of soluble dyes used by the textile industry as their tinctorial value is very high.

Wastewaters from dyeing industries are released in to 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 also have certain disadvantages. The adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed 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 (Selvarani, 2000; Sekaran et al., 1995). The present study is undertaken to evaluate the efficiency of a carbon adsorbent prepared from acid activated Pandanus carbon (PDC) for removal of dye in aqueous solution. In order to design on adsorption treatment system, knowledge of the 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 (CR), Malachite green (MG) and Rhodamine B (RDB) onto activated carbon.

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**Table 1.** Equilibrium parameters for the adsorption of dyes onto activated carbon.

[D]0	Ce (mg/L)				Qe (mg/g)				Dye removed (%)			
Temperature (°C)												
	30	40	50	60	30	40	50	60	30	40	50	60
<b>CR adsorption</b>												
5	1.2520	1.0281	0.9256	0.8351	1.874	1.985	2.037	2.082	74.96	79.43	81.48	83.30
10	2.5780	2.2528	2.0281	1.9821	3.711	3.874	3.986	4.009	74.22	77.47	79.71	80.18
15	4.7812	4.2121	4.0121	3.8559	5.109	5.394	5.494	5.572	68.13	71.92	73.25	74.29
20	7.8521	7.2821	7.0421	6.8529	6.074	6.359	6.479	6.574	60.74	63.59	64.79	65.74
25	11.2821	10.9251	10.4281	9.5790	6.859	7.037	7.286	7.711	54.87	56.30	58.29	61.68
30	14.7281	14.2832	14.059	13.1512	7.636	7.858	7.971	8.424	50.81	52.39	53.14	56.16
<b>MG adsorption</b>												
5	1.4852	1.3456	1.2012	1.1015	1.7574	1.8272	1.8994	1.9492	70.29	73.08	75.97	77.97
10	3.5793	3.1527	3.3116	3.2012	3.2100	3.2750	3.3442	3.3994	64.20	68.47	68.84	67.98
15	6.1863	6.0137	5.9452	5.8124	4.4088	4.4934	4.5274	4.5938	58.78	59.91	60.36	61.25
20	9.2245	9.0192	8.9921	8.7529	5.3877	5.4904	5.5039	5.6239	53.87	54.90	55.03	56.23
25	12.9348	12.8015	12.8015	12.5029	6.0326	6.0992	6.1937	6.2485	48.26	48.79	49.54	49.98
30	16.4996	16.2856	16.1252	16.0021	6.7502	6.8572	6.9372	6.9989	45.00	45.71	46.24	46.65
<b>RDB adsorption</b>												
5	2.2592	2.0152	1.9222	1.7556	1.3704	1.4924	1.5389	1.6222	54.81	59.69	61.55	64.88
10	4.5396	4.2346	3.9846	3.5998	2.7302	2.8827	3.0077	3.2001	54.60	57.65	60.15	64.00
15	7.4325	7.2498	7.0326	6.8932	3.7837	3.8751	3.9837	4.0534	50.45	51.66	53.11	54.04
20	10.5498	10.1235	9.7256	9.0352	4.7251	4.9382	5.1372	5.4824	47.25	49.38	51.37	54.82
25	14.5926	14.0236	13.8556	13.5452	5.2037	5.4882	5.5722	5.7244	41.62	43.90	44.57	45.81
30	17.8445	17.4452	17.0282	16.8556	6.0777	6.2774	6.4859	6.5722	40.51	41.84	43.23	43.81

## MATERIALS AND METHODS

### Materials

Dried leaves of Pandanus were carbonized with concentrated sulphuric acid in the weight ratio of 1:1(W/V). The carbonization and activation was completed by heating for twelve hours in a furnace at 400°C. 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 100°C in a hot air oven. The dried material was ground well to a fine powder and sieved.

All chemicals used were of high purity, commercially available **AnalaR** grade. Stock solutions of 1g/L of dyes were prepared using doubly distilled water.

### Methods

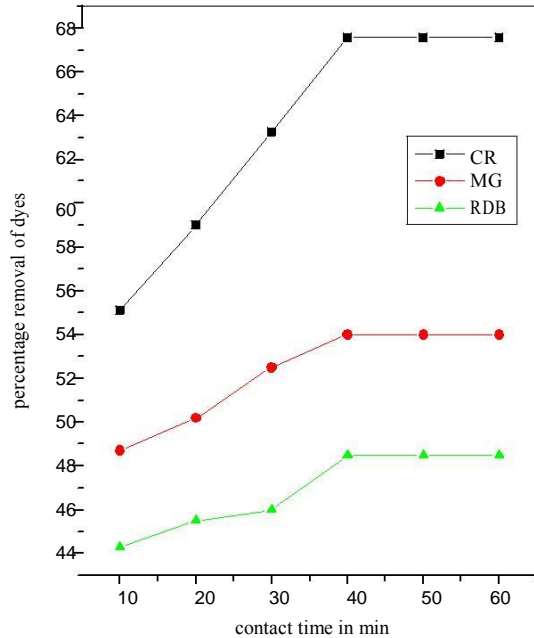
Congo red (CR), Malachite green (MG) and Rhodamine B (RDB) dyes solutions were made to a known concentration. From that, 50 ml of 5, 10, 15, 20, 25 and 30 mg/L dye solutions were taken and loaded with the 100 mg of activated carbon adsorbent. Then these were agitated at 30°, 40°, 50°, and 60°C in defined time intervals. After that samples were withdrawn from the shaker and filtered. Then there were analyzed in UV-Visible spectrophotometer.

Desorption studies were carried out using the spent carbon. The carbon loaded with dyes was separated and gently washed with distilled water to remove any unadsorbed dyes. Each of the dye-laden carbons was agitated with 50 ml of water, 0.2 M sulphuric acid, hydrochloric acid, and nitric acid and sodium chloride solutions separately for 30 min and analyzed.

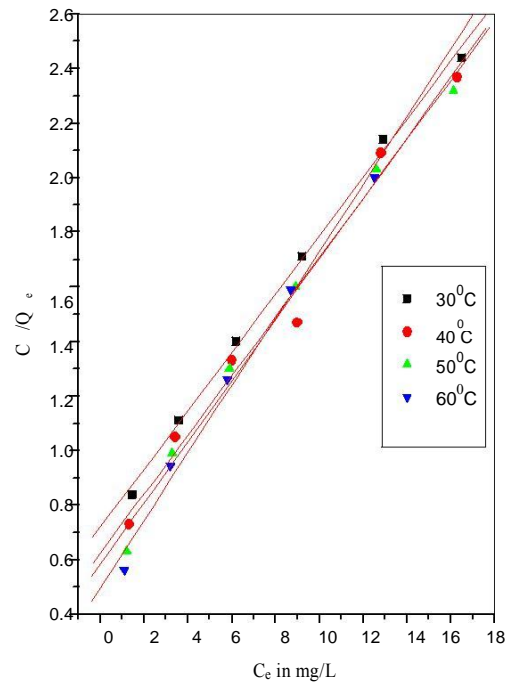
## RESULTS AND DISCUSSIONS

### Effect of contact time and initial dye concentration

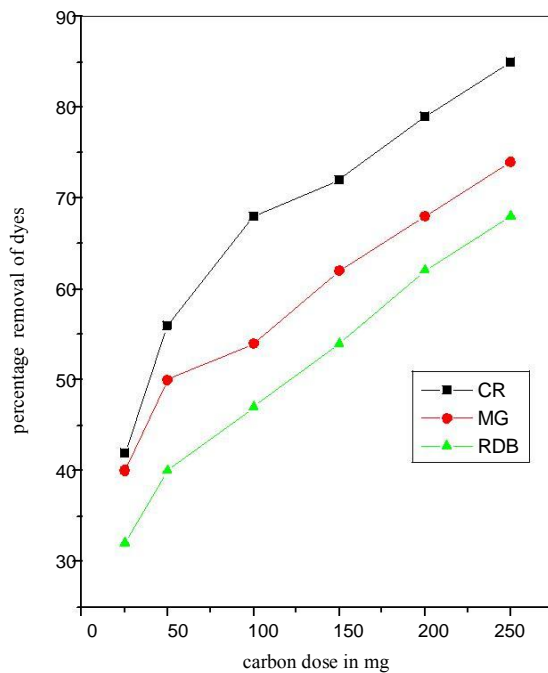
The experimental results of adsorptions of Congo red (CR), Malachite green (MG) and Rhodamine B (RDB) on the activated carbon at various initial concentrations (5, 10, 15, 20, 25 and 30 mg/L) with contact time are shown in Figure 1 and Table 1. The equilibrium data are collected in Table 1 reveal that the percent adsorption decreases with the increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of carbon increased with increase in dyes concentration. It means that the adsorption is highly dependent on the initial concentration of dyes. This is because at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low, subsequently, the fractional adsorption become independent on the initial concentration. However, at high concentration the available sites of adsorption becomes fewer, and hence, the percentage removal of dye is dependent upon the initial concentration. The equilibrium is established within 40 min for all concentrations. Figure 1 reveals that the curves are smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dyes on the carbon surface (Senthikumar et al., 2005).



**Figure 1.** Effect of contact time on the adsorption with the initial concentration of 20 mg/L.



**Figure 3.** Langmuir isotherm for the adsorption of MG by PDC.



**Figure 2.** Effect of the dosage (carbon load) on the removal of dyes.

**Effect of carbon concentration**

The adsorption of the dyes on carbon is studied by varying the carbon concentration (1 – 5 mg/ml) for Congo red (CR), Malachite green (MG) and Rhodamine B (RDB)

concentrations of 20 mg/L. The percentage of adsorption increases with increase in the carbon concentration (Figure 2). This is attributed to increased carbon surface area and availability of more adsorption sites.

**Adsorption isotherm**

The experimental data are analyzed according to the linear form of the Langmuir and Freundlich isotherms.

The Langmuir isotherm is represented by the following equation (Langmuir and Amer, 1918).

$$C_e/Q_e = 1/Q_m b + C_e / Q_m \dots \dots \dots (1)$$

Here  $C_e$  is the equilibrium concentration (mg/L),  $Q_e$  is the amount adsorbed at equilibrium (mg /g) and  $Q_m$  and  $b$  are Langmuir constants related to the 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 (Figure 3). The values of  $Q_m$  and  $b$  are determined from the slope and intercept of the plots and are presented in Table 2. From the results, it is clear that the values of adsorption efficiency  $Q_m$  and adsorption energy  $b$  of the carbon vary with increasing the temperature. From the values we can conclude that the maximum adsorption corresponds to a saturated mono-layer of adsorbate molecules on an adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface occurs. The trend shows that the adsorbent prefers to bind acidic ions and that specia-

**Table 2.** Langmuir isotherm results.

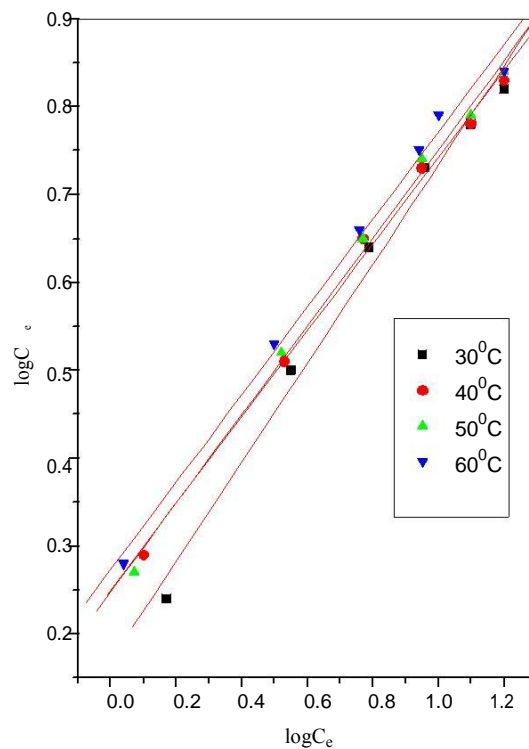
Dyes	Temp <sup>o</sup> C	Statistical parameters/constants		
		r	Qm	b
CR	30	0.9926	21.4915	0.2339
	40	0.9946	20.2675	0.2792
	50	0.9936	20.0680	0.3196
	60	0.9917	18.9286	0.4145
MG	30	0.9990	9.7377	0.1364
	40	0.9919	9.6246	0.1626
	50	0.9989	9.6339	0.1560
	60	0.9981	9.5693	0.1650
RDB	30	0.9865	10.6723	0.0712
	40	0.9945	10.3412	0.0862
	50	0.9646	9.4876	0.1228
	60	0.9234	10.7066	0.0882

**Table 3.** Dimensionless Separation factor (RL)

[D]0 (mg / L)	Temperature (°C)			
	30	40	50	60
<b>CR adsorption</b>				
5	0.4609	0.4166	0.3846	0.3257
10	0.2994	0.2631	0.2380	0.1945
15	0.2222	0.1923	0.1724	0.1386
20	0.1763	0.1519	0.1351	0.1077
25	0.1461	0.1254	0.1111	0.0881
30	0.1248	0.1067	0.0943	0.0745
<b>MG adsorption</b>				
5	0.5882	0.5555	0.5617	0.5494
10	0.4166	0.3846	0.3906	0.3773
15	0.3225	0.2941	0.2994	0.2881
20	0.3225	0.2941	0.2994	0.2881
25	0.2631	0.2380	0.2427	0.2325
30	0.1923	0.1724	0.1760	0.1680
<b>RDB adsorption</b>				
5	0.7407	0.6993	0.6250	0.6451
10	0.5882	0.5373	0.4545	0.4761
15	0.4854	0.4348	0.3571	0.3773
20	0.3610	0.3174	0.2500	0.2666
25	0.3610	0.3174	0.2500	0.2666
30	0.3194	0.2793	0.2173	0.2325

tion predominates on sorbent characteristics, when ion exchange is the predominant mechanism. Further, it confirms the endothermic nature of the processes involved in the system. To confirm the favorability of the adsorption process, the separation factor ( $R_L$ ) is calculated and presented in Table 3. The values are found to be between 0 and 1 and confirm that the ongoing adsorption process is favourable (Khattri and Singh, 1999).

$$R_L = 1 / (1 + bC_0) \dots \dots \dots (2)$$



**Figure 4.** Freundlich isotherm for the adsorption of MG by PDC.

Here,  $b$  is the Langmuir constant and  $C_0$  is the initial concentration of the dye.

The Freundlich equation is also employed for the adsorption of Congo red (CR), Malachite green (MG) and Rhodamine B (RDB) dyes on the adsorbent. The Freundlich isotherm (Freundlich, 1906) is represented as

$$\log Q_e = \log K_f + 1/n \log C_e \dots \dots \dots (3)$$

Here  $Q_e$  is the amount of Congo red (CR), Malachite green (MG) and Rhodamine B (RDB) adsorbed (mg/g),  $C_e$  is the equilibrium concentration of dye in the solution (mg/L) and  $K_f$  and  $n$  are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plot of  $\log Q_e$  versus  $\log C_e$  shows that the adsorption of CR, MG and RDB dye follows also the Freundlich isotherm (Figure 4). The values of  $K_f$  and  $n$  found and given in Table 4, shows the increase of negative charge on the surface that enhances the electrostatic force between the carbon surface and the dye ion, which increases in turn the adsorption of dyes. The values clearly show the dominance of adsorption capacity. The intensity of adsorption is an indication for the bond energies between dye and the adsorbent and the possibility of a slight chemisorption rather than physisorption. The possibility of multilayer adsorption of dyes through the percolation process cannot be ruled out. However, the values of  $n$  is greater than one indicating

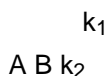
**Table 4.** Freundlich isotherm results.

Dyes (mg/L)	Temp °C	statistical parameters/constants		
		r	K <sub>f</sub>	N
<b>CR</b>				
	30	0.9894	1.8047	1.4074
	40	0.9900	1.8648	1.4560
	50	0.9887	1.9340	1.4764
	60	0.9762	2.0301	1.5304
<b>MG</b>				
	30	0.9963	1.2711	2.0303
	40	0.9900	1.2996	2.0735
	50	0.9984	1.3322	2.1502
	60	0.9970	1.3586	2.1940
<b>RDB</b>				
	30	0.9956	1.0546	1.6843
	40	0.9981	1.4173	2.8208
	50	0.9958	1.1834	1.8667
	60	0.9862	1.2881	2.1043

that the adsorption is much more favourable (MaKay et al., 1982)

**Kinetics of adsorption**

The 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 dyes removal was carried out to understand the behaviour of this low cost carbon adsorbent. The adsorption of dyes from an aqueous solution follows a reversible first order kinetics, when a single species are considered on a heterogeneous surface. The heterogeneous equilibrium between the dye solution and the activated carbon is expressed as:



Here  $k_1$  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 calculated as earlier (Weber, 1967; Kocke and Hemphill, 1981). The data given in Table 5 show that the forward rate constant is much higher than the backward rate constant suggesting that the adsorption rate is clearly dominant. At equilibrium, the rate is the ratio of the concentration of adsorbate in adsorbent and concentration of adsorbate in aqueous solution given by  $K_0$ . The calculated values are presented in the Table 6. The re-

sults indicate that  $K_0$  decreases with the increase in the concentration of dyes and increases with the increase in temperature

Examination of the effect of dye concentrations on the rate constant  $K_{ad}$  (Table 5), the values helps to understand the mechanism of dye removal (Weber, 1967). In the case of strict surface adsorption, the variation of the adsorption rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between the initial dye concentration and rate of reaction will not be linear (Kocke and Hemphill, 1981).

**Effect of temperature**

The adsorption capacity of the carbon increases with the increase in the temperature of the system from 30° to 60°C. The thermodynamic parameters such as change in free energy ( $G^\circ$ ) KJ/mol, enthalpy ( $H^\circ$ ) KJ/mol and entropy ( $S^\circ$ ) J/mol are determined using the following equations (Catena and Bright, 1989)

$$K_0 = C_{solid}/C_{liquid} \dots \dots \dots (4)$$

$$G^\circ = -RT \ln K_0 \dots \dots \dots (5)$$

$$\log K_0 = S^\circ / (2.303RT) - H^\circ / (2.303RT) \dots \dots \dots (6)$$

Here  $K_0$  is the equilibrium constant,  $C_{solid}$  is the solid phase concentration at equilibrium (mg/ L),  $C_{liquid}$  is the liquid phase dye concentration at equilibrium (mg/L), T is the temperature in Kelvin and R is the universal gas constant. The values  $H^\circ$  and  $S^\circ$  obtained from the slope and intercept of Van't Hoff plots have presented in Table 6. The values are the range of 1 to 93 KJ/mol indicating the favourability of physisorption. From the order we could conclude that physisorption is much more favourable for CR. The positive values of  $H^\circ$  show the endothermic nature of adsorption and the possibility of physical adsorption. In the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption increases, this rules out the possibility of chemisorptions. However, the very low  $H^\circ$  value shows that the dye is physisorbed onto the adsorbent (McKay and Poots, 1980)

The negative values of  $G^\circ$  (Table 6) show that the adsorption is highly favourable for CR. However, it indicates that the dye adsorption is spontaneous. The positive values of  $S^\circ$  (Table 6) show increased disorder and randomness at the solid solution interface of the adsorbent PDC. During the adsorption there, some structural changes in the dyes and the adsorbent occur.

The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational entropy than it is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system (Namasiva-

**Table 5.** Rate constants for the adsorption of dyes ( $10^3 k_{ad}, \text{min}^{-1}$ ) and the constants for forward ( $10^3 k_1, \text{min}^{-1}$ ) and reverse ( $10^3 k_2, \text{min}^{-1}$ ) process.

[D]0	Temperature (°C)											
	kad				30		40		50		60	
	30	40	50	60	k1	K2	k1	K2	k1	K2	k1	K2
<b>CR adsorption</b>												
5	2.8902	3.5788	4.1914	4.5852	9.9472	0.4885	12.5274	0.5007	12.130	0.5014	14.727	0.499
10	19.0987	19.7459	21.4317	21.5692	7.7931	3.7158	8.9960	3.5961	9.471	3.6461	10.039	3.426
15	15.8653	17.2425	18.7579	20.0084	5.0346	3.7158	5.5651	3.5961	7.992	3.8629	7.052	3.796
20	10.8056	9.3732	12.0331	12.6503	3.6369	3.5079	4.1181	2.8987	4.551	3.5775	4.404	3.604
25	9.2649	9.3729	10.0529	10.3034	4.4569	3.4215	4.6042	3.3182	5.074	3.3946	2.985	3.300
30	7.3995	8.2355	8.5291	8.7168	3.2695	3.0724	3.5221	3.2003	3.595	3.2696	2.659	3.235
<b>MG adsorption</b>												
5	16.950	14.467	15.402	16.121	11.91	5.044	10.58	3.890	11.70	3.701	12.57	3.550
10	6.909	8.659	9.073	9.212	4.43	2.476	5.94	3.138	5.79	2.864	6.26	2.952
15	6.909	7.945	8.083	4.606	4.05	2.855	4.76	3.188	4.88	3.206	2.76	1.844
20	6.448	6.448	6.909	4.606	3.46	2.981	3.53	2.914	3.79	3.112	2.02	2.047
25	6.218	5.941	4.606	6.909	3.01	3.216	2.70	3.046	2.28	2.323	3.45	3.455
30	5.987	5.757	5.987	6.909	2.69	3.293	2.63	3.206	3.78	3.206	3.21	3.695
<b>RDB adsorption</b>												
5	8.498	10.363	9.465	10.616	4.65	3.84	5.64	3.81	6.28	4.08	6.89	3.72
10	6.425	6.586	7.277	7.599	3.50	2.92	3.80	2.78	4.32	2.89	4.82	2.73
15	4.447	5.365	8.981	6.909	2.24	2.20	2.76	2.60	4.59	4.21	3.73	3.17
20	4.030	3.408	4.836	4.444	1.69	2.34	1.50	1.91	2.15	2.68	2.03	2.41
25	4.030	3.408	4.836	4.444	1.69	2.34	1.50	1.91	2.15	2.68	2.03	2.41
30	5.296	5.757	5.987	6.033	2.14	3.14	2.41	3.34	2.59	3.39	2.65	3.38

**Table 6.** Equilibrium constant and thermodynamic parameters for the adsorption of dyes onto carbon.

[D]0	K0		$\Delta G^\circ$						$\Delta H^\circ$	$\Delta S^\circ$
	Temperature (C)									
	30°	40°	50°	60°	30°	40°	50°	60°		
<b>CR adsorption</b>										
5	2.9936	3.8633	4.4019	4.9873	-2.761	-3.517	-3.979	-4.445	13.895	55.21
10	2.8789	3.4389	3.9309	4.0451	-2.663	-3.213	-3.675	-3.867	9.709	41.05
15	2.1372	2.5611	2.7386	2.8901	-1.913	-2.446	-2.704	-2.937	8.170	33.52
20	1.5470	1.7464	1.8399	1.9184	-1.098	-1.449	-1.635	-1.803	5.855	23.10
25	1.2158	1.2883	1.3973	1.6098	-0.491	-0.659	-0.896	-1.317	7.591	26.49
30	1.0369	1.1003	1.1338	1.2811	-0.091	-0.247	-0.335	-0.683	5.461	18.22
<b>MG adsorption</b>										
5	2.3670	2.717	3.1660	3.5450	-2.170	-2.591	3.088	-3.487	11.282	44.39
10	1.7966	1.8939	2.0210	1.7830	-1.466	-1.665	-1.887	-2.078	4.788	20.64
15	1.4260	1.4940	1.5250	1.5840	-0.891	-1.043	-1.130	-1.270	2.515	12.26
20	1.1682	1.2178	1.2250	1.2550	-0.390	-0.509	-0.530	-0.680	2.286	8.85
25	0.9334	0.9531	0.9820	1.0000	+0.171	+0.124	+0.053	+0.000	1.928	5.79
30	0.8182	0.8427	0.8650	0.8750	-0.091	+0.444	+0.402	+0.368	1.912	4.67
<b>RDB adsorption</b>										
5	1.2131	1.4812	1.6041	4.9873	-0.486	0-1.021	-1.268	-1.705	11.215	38.80
10	1.2028	1.3614	1.5125	1.7830	-0.465	-0.802	-1.109	-1.509	10.680	36.72
15	1.0181	1.0690	1.1330	1.5840	-0.044	-0.046	-0.335	-0.450	4.102	13.69
20	0.8957	0.9756	1.0576	1.2148	+0.277	+0.065	-0.147	-0.535	8.247	26.21
25	0.7164	0.7827	0.8050	0.8463	+0.838	+0.637	+0.582	+0.459	4.489	12.18
30	0.6816	0.7201	0.7626	0.8750	+0.969	+0.853	+0.727	+0.686	3.89	9.69

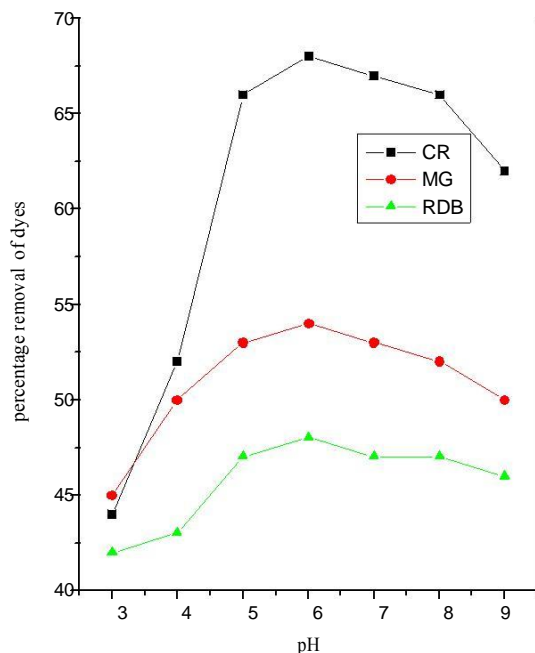


Figure 5. Effect of pH on the removal of dyes

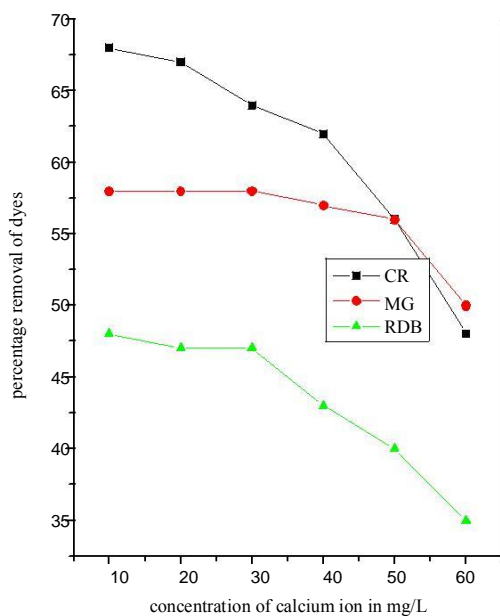


Figure 6. Effect of calcium ion on the removal of dyes.

yam and Yamuna, 1995). From the results, we could conclude that more efficient is the physisorption. The enhancement of adsorption capacity of the activated carbon at higher temperatures is attributed to the enlargement of pore size and activation of the adsorbent surface (Senthilkumar et al., 2005).

## Effect of pH

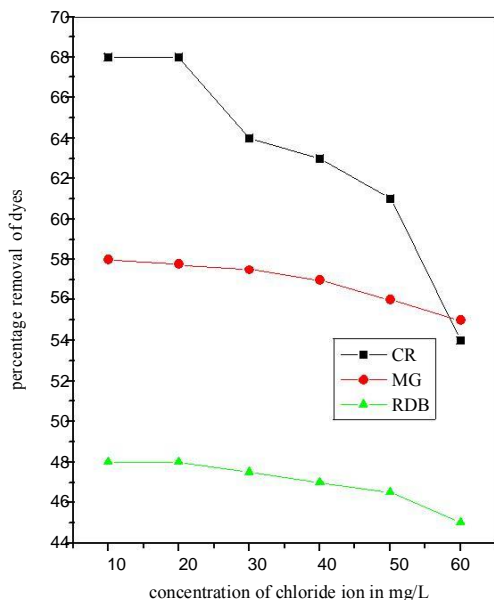
The experiments carried out at different pH show that there is a change in the percent removal of dyes over the entire pH range of 3 to 9 shown in the Figure 5. This indicates the strong force of interaction between the dyes and the activated carbon that, either  $H^+$  or  $OH^-$  ions could influence the adsorption capacity. Here the interaction is larger at pH 6 due to the competence of acidic  $H^+$  ion with dye cation for the sorption sites. The percentage of sorption increases above this pH value due to the presence of ionic COOH groups. The adsorption of dyes on the activated carbon does involve ion exchange mechanism. Due to this mechanism there should be an influence on the dye adsorption while varying the pH. This observation is in line with the type I isotherm shown in Figure 3 and 4. The positive  $H^0$  value obtained, which indicates irreversible adsorption probably due to polar interaction (Sivaraj et al., 2001).

## Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dyes. If the adsorbed dyes can be desorbed using neutral pH water, then the attachment of the dyes on the adsorbent is weak. If sulphuric acid or alkaline water desorb the dyes, then the adsorption is by ion exchange. If organic acids, like acetic acid desorb the dyes, then the dye is attached to the adsorbent through chemisorption (Namasivayam et al., 1995). The effect of various reagents used for desorption studies shows that hydrochloric acid is a better reagent for desorption, because we could get more than 90% removal of adsorbed dyes. The reversibility of adsorbed dyes in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of dyes by mineral acids and alkaline medium indicates that the dyes are adsorbed onto the activated carbon by physisorption.

## Effect of other ions

The effect of other ions like  $Ca^{2+}$  and  $Cl^-$  on the adsorption process is studied at different concentrations. The ions added are to 20 mg/L of dye solutions and the contents are agitated for 60 min at  $30^0C$ . The results shown in Figure 6 and 7 reveal that low concentration of  $Cl^-$  does not affect the percentage of adsorption of dyes on activated carbon, because the interaction of  $Cl^-$  at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of  $Ca^{2+}$  ion increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption increases which decreases the percentage of adsorption. The interference is more in the presence of  $Ca^{2+}$  compared with  $Cl^-$  ion. This is so because ions with smaller hydrated radii decrease the swelling pressure in the



**Figure 7.** Effect of chloride ion on the removal of dyes.

sorbent and increase the affinity of the sorbent to such ions (Anuirudhan and Sreedhar, 1999).

## CONCLUSIONS

The experimental data correlated reasonably well with the Langmuir and Freundlich adsorption isotherms and the respective isotherm parameters are calculated. The amount of dyes adsorbed increases with the increase in pH of the medium. The amount of the adsorbed Congo red, Malachite green and Rhodamine B slightly decrease with increasing the ionic strength and increase with the increase in temperature. The dimensionless separation factor shows that the activated carbon can be used for the removal of Congo red, Malachite green and Rhodamine B from aqueous solution. The values of  $H^\circ$ ,  $S^\circ$  and  $G^\circ$  shows that the employed carbon has a considerable potential as an adsorbent for the removal of Congo red, Malachite green and Rhodamine B.

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