September 2007 Volume 2 Issue 3

Trade Science Inc.

Environmental Science

An Indian Journal

Current Research Paper

ESAIJ, 2(3), 2007 [176-186]

Equilibrium, Kinetic And Thermodynamic Studies On The Adsorption Of Anionic And Cationic Dyes Onto A Low Cost Activated Carbon

K.P.Elango*, S.Arivoli, M.Sundaravadivelu
Department of Chemistry, Gandhigram Rural University, Gandhigram-624 302, (INDIA)
E-mail : drkpelango@rediffmail.com

Received: 21th May, 2007 ; Accepted: 26th May, 2007

ABSTRACT

Batch sorption system using activated carbon from a herb source as an adsorbent was investigated to remove Congo red, Malachite green; Rhodamine B and Rose Bengal dyes from aqueous solutions. The system variables studied include initial concentration of the sorbate, agitation time, adsorbent dose, pH, co-ions and temperature. The experimental data fitted well to the Langmuir and Freundlich isotherms. Thermodynamic parameters such as ΔH^0, ΔS^0 and ΔG^0 were calculated indicating that the adsorption was a spontaneous, endothermic and a physical process. Kinetic studies reveal that the adsorption is first order. A mechanism involving two stages has been proposed for the adsorption of dyes onto the adsorbent. FT-IR, and SEM patterns of the adsorbent were recorded to get a better in sight into the mechanism of the adsorption process.

KEYWORDS

Dyes;
Activated carbon;
Adsorption isotherms;
Kinetics;
Thermodynamics.

INTRODUCTION

Industrial effluents are one of the major causes of environmental pollution. Effluents discharged from dyeing industries are highly coloured[1]. Due to their chemical structure, dyes are resistant to light, many chemicals, oxidizing agents, and heat and are biologically non degradable and therefore difficult to decolorize once released into the aquatic environment[2]. Disposal of this colored water into receiving waters can be toxic to aquatic life. It may be mutagenic and carcinogenic and can cause severe damage to human beings, such as dysfunction of the kidneys, reproductive system, liver, and brain and central nervous system. Wastewater containing dyes from the textile industry is very difficult to treat using conventional wastewater treatment methods, which are coagulation, ultra filtration, ozonation, oxidation, sedimentation, reverse osmosis, flotation, precipitation, etc., due to economic considerations. Adsorption has gained favour in recent years due to proven efficiency in the removal of pollutants from effluents to stable forms for the above conventional treatment methods[3].

Wastewater-contained molecules have attached to the surface of the adsorbent and this interaction may express in terms of both adsorptive characteristics and physical properties. Several researchers have carried out the successful removal of dyes with activated carbon. Activated carbon is a widely used adsorbent due to its high adsorption capacity, high surface area, microporous structure, and high degree of surface reactivity, but there are some problems with its use. It is expensive and regeneration using solution procedures requires a small additional effluent, while regeneration results in a 10-15% loss of adsorbent and its uptake capacity and therefore this adds to the operational cost. This led to a search for cheaper, easily obtainable materials for the adsorption of dye[4]. The present study, therefore, was focused on Congo red, Malachite green; Rhodamine B and Rose Bengal adsorption equilibrium. The objective of the present work was to study the kinetics and thermodynamics and to determine dye sorption capacity of active carbon obtained from *Aegle marmelos (Linn.) fruit*. This plant was selected to prepare the carbon due to its medicinal nature and its availability throughout India.

EXPERIMENTAL PROCEDURES

Materials

All the reagents used were of commercially available high purity Analar grade(SRL, Sd-fine, India). Stock solutions of dyes were prepared by dissolving high purity Analar grade dyes in doubly distilled water.

Preparation of active carbon

The fruits of *Aegle marmelos(Linn.)* were procured locally, crushed, washed thoroughly with water to remove dust and dried naturally. The active carbon was prepared by treating the dried material with sulphuric acid(1:1 w/v). The carbonized material was washed with distilled water to remove excess of acid and activated at 400^{0}C in a furnace. Grinding the material, followed by sieving gave the adsorbent.

The pH at the potential of zero charge(pH$_{zpc}$) of the activated carbon as measured using the pH drift method[5]. The selective neutralization method used to evaluate the amphoteric character of the carbon surface was the scheme suggested by Boehm[5].

Methodology

The concentration of dyes was measured using UV-Vis double beam spectrophotometer (Shimadzu, Graphicord 240). The particle size of the adsorbent was determined using the Carl Zeiss Light microscope (Axiostar Plus) as reported earlier[6]. The FT IR spectra of was recorded in a JASCO FT-IR 460 Plus spectrometer. The SEM images of the adsorbent were obtained from Central Electrochemical Research Institute, Karaikudi.

Batch adsorption experiments

Adsorption experiments were performed by agitating 250mg of adsorbent with 50 ml of dye solution of desired concentrations at 30±1^{0}C in different stoppered bottles in a shaking thermostat machine. At the end of pre-determined time intervals, the sorbate was filtered and the concentration of dye was determined. All experiments were carried out twice and the average values are given. Experimental variables considered were: **(i)** Initial concentration of dyes: 10-60mg L^{-1} ; **(ii)** Contact time between adsorbent and the dyes solution: 5-60min ; **(iii)** pH: 3-10 ; **(iv)** Dosage of the adsorbent: 50-1500mg/50ml ; and **(v)** temperature: 30-60^{0}C.

For desorption study the dye loaded adsorbent was agitated with 50mL each of hydrochloric acid, nitric acid, sodium chloride, mixture of sodium chloride and hydrochloric acid (all 0.2M) and water for an hour, filtered and the filtrate was analyzed for the dye.

Data analysis

The experimental data were analyzed using Microcal Origin(version 6) computer software. The goodness of fit was discussed using correlation coefficient r, and standard deviation, sd.

RESULTS AND DISCUSSION

Sorbent characterization

The activated carbon was characterized by conventional chemical and analytical methods. The important characteristics of the adsorbent thus obtained are collected in TABLE 1. The graph of final pH versus initial pH obtained using the pH drift method for the active carbon is shown in figure 1.

Titration studies

According to Boehm[5], only the strongly acidic carboxylic acid groups are neutralized by $NaHCO_3$, where as those neutralized by Na_2CO_3 are thought to be lactone, lactol and carboxyl group. The weakly acidic phenolic groups only react with strong alkali NaOH. Therefore, by selective neutralization using bases of different strength, the surface acidic functional groups in carbon can be characterized both quantitatively and qualitatively. Neutralization with HCl characterizes the amount of surface basic groups that are, for example, pyrones and chromenes. The basic properties are described to surface basic groups and the π electron system of carbon basal planes. Selective neutralization studies show that the amounts(in m equiv/g) of $NaHCO_3$, Na_2CO_3, NaOH and HCl consumed by the carbon are 0.281, 0.074, 0.121 and 0.056 respectively. These results along with pH_{zpc} value indicate that the carbon may contain acidic oxygen functional groups[5,7].

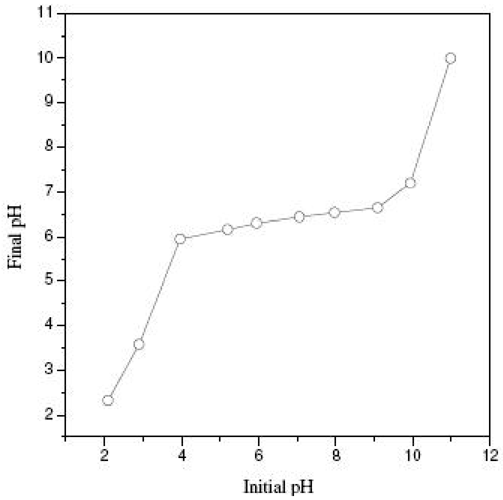

Figure 1 : pHzpc curve for the adsorbent AMC

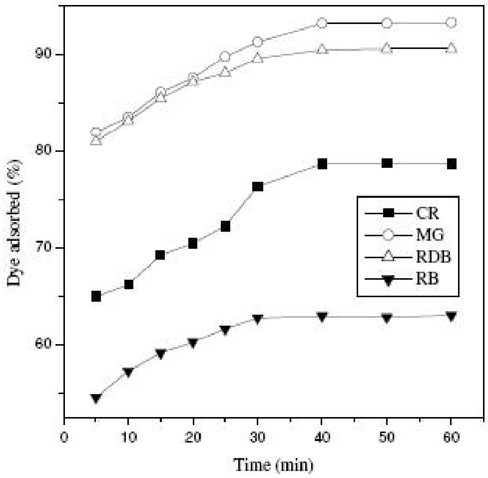

Figure 2 : Effect of contact time on the adsorption of dyes onto AMC

[Dye]=20mg/L; pH=7; Temp=30^{0}C

TABLE 1 : Characteristics of the adsorbent

Properties	Activated carbon (AMC)
Particle size(mm)	0.17
Density(g/cc)	0.5855
Moisture content(%)	1.50
Loss on ignition(%)	90.5
Acid insoluble matter(%)	3.0
Water soluble matter(%)	0.21
pH of aqueous solution	6.8
pH_{ZPC}	6.3
Surface groups (m equiv/g)	
i) Carboxylic acid	0.281
ii) Lactone, lactol, carboxyl	0.074
iii) Phenolic	0.121
iv) Basic (pyrones and chromenes)	0.056

Effect of agitation time and initial concentration

The experimentally measured equilibrium parameters and the amount of dyes adsorbed are given in TABLE 2. Figure 2 shows the progression of adsorption reaction, the percentage removal of dyes by AMC after different contact times. As contact time was increased, initially, percentage removal also increased, but after some time, it gradually approached an almost constant value, denoting attainment of equilibrium. It was assumed that the equilibrium time is that at which curves appear nearly asymptotic to the time axis. In the present case, the equilibrium time was obtained at 40 min for AMC. The changes in the rate of removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Later, the dye uptake rate by adsorbent had decreased significantly, due to the decrease in number of adsorption sites. Decreased removal rate, particularly, towards the end of experiment, indicates the possible monolayer of dye on the outer surface, pores of the adsorbent and pore diffusion onto inner surface of

TABLE 2 : Equilibrium parameters for the adsorption of dyes ions onto activated carbon

$[D]_0$	C_e (mg L^{-1})				Q_e (mg g^{-1})				Dye removed (%)			
	30^0	40^0	50^0	60^0	30^0	40^0	50^0	60^0	30^0	40^0	50^0	60^0
10	1.88	1.84	1.80	1.76	1.62	1.63	1.64	1.65	81.2	81.6	82.0	82.4
20	4.26	4.10	3.95	3.71	3.15	3.18	3.21	3.26	78.7	79.5	80.3	81.4
30	6.57	6.25	5.94	5.63	4.69	4.75	4.81	4.87	78.1	79.2	80.2	81.2
40	10.83	10.44	10.05	9.70	5.83	5.91	5.99	6.06	72.9	73.9	74.9	75.8
50	14.93	14.46	14.00	13.53	7.01	7.11	7.20	7.29	70.1	71.1	72.0	73.0
60	22.17	21.58	21.38	20.80	7.57	7.68	7.72	7.84	63.0	64.0	64.4	65.3
Malachite green adsorption												
10	0.65	0.62	0.59	0.55	1.87	1.88	1.88	1.89	93.5	93.8	94.1	94.5
20	1.37	1.31	1.25	1.19	3.73	3.74	3.75	3.76	93.2	93.5	93.8	94.1
30	2.43	2.26	2.14	1.98	5.51	5.55	5.57	5.60	91.9	92.5	92.8	93.4
40	4.22	4.02	3.84	3.64	7.16	7.20	7.23	7.27	89.5	89.9	90.4	90.8
50	6.58	6.29	5.95	5.73	8.68	8.74	8.81	8.85	86.9	87.4	88.1	88.5
60	8.41	8.07	7.68	7.35	10.32	10.39	10.46	10.53	85.9	86.5	87.2	87.7
Rhodamine B adsorption												
10	0.88	0.82	0.76	0.69	0.91	0.92	0.92	0.93	91.2	91.8	92.4	93.1
20	1.87	1.74	1.67	1.47	1.81	1.83	1.83	1.85	90.6	91.3	91.6	92.6
30	3.78	3.60	3.33	3.15	2.62	2.64	2.67	2.69	87.4	87.9	88.8	89.5
40	5.26	5.23	5.09	4.90	3.47	3.48	3.49	3.51	86.8	86.9	87.3	87.8
50	12.59	12.22	11.81	11.52	3.74	3.78	3.82	3.84	74.8	75.6	76.4	76.9
60	16.21	15.73	15.26	14.84	4.37	4.43	4.47	4.52	72.9	73.7	74.6	75.3
10	4.28	4.00	3.63	3.38	0.29	0.30	0.32	0.33	57.2	59.9	63.7	66.2
20	7.42	6.55	5.95	5.62	0.63	0.67	0.70	0.72	62.9	67.2	70.2	71.9
30	13.13	12.60	11.92	11.39	0.84	0.87	0.90	0.93	56.2	57.9	60.3	62.0
40	21.04	19.80	18.59	17.90	0.95	1.01	1.07	1.10	47.4	50.5	53.5	55.2
50	26.50	25.23	24.02	23.25	1.17	1.24	1.30	1.34	46.9	49.5	51.9	53.5
60	36.37	34.37	32.80	31.50	1.18	1.28	1.36	1.42	39.4	42.7	45.3	47.5

adsorbent particles through the film due to continuous shaking maintained during the experiment[8].

Effect of adsorbent dose

The effect of adsorbent dosage on adsorption of dyes at pH 7 and contact time 60min for the adsorbent was studied. The results are presented as percentage removal of dyes versus adsorbent dosage in figure 3. Adsorbent dose was varied from 50mg to 1500mg per 50ml. From the result it is evident that optimum adsorbent dosage of 250mg for Congo red and malachite green, 500mg for rhodamine B and 1000mg for rose Bengal is required for appreciable removal and these values were fixed as the doses for further studies.

Adsorption isotherms

The adsorption isotherms generally used for the design of adsorption system. The Langmuir[9] and Freundlich[10] equations are commonly used for describing the adsorption isotherm. The linear equation of Langmuir and Freundlich are represented as follows Eqs. (1) and (2), respectively.

$$C_e/Q_e=(C_e/Q^0)+(1/Q^0b) \quad (1)$$

$$\log Q_e=1/n \log C_e+\log K \quad (2)$$

Where Q_e and C_e has the usual meanings and Q^0 and b are the Langmuir constants, indicating the adsorption capacity and energy of adsorption respectively. K and n are the empirical constants of the Freundlich isotherm measuring the adsorption capacity and intensity of adsorption respectively.

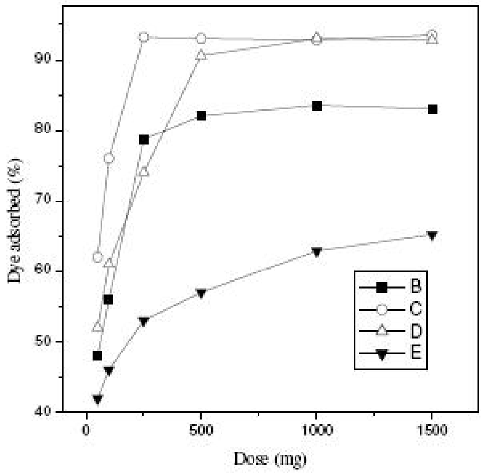

Figure 3 : Effect of adsorbent dose on the adsorption of dyes onto AMC

[Dye]=20mg/L; Temp=30^0C; pH=7; Contact time=60min

To quantify the adsorption capacity of the chosen adsorbent for the removal of dyes, the Langmuir adsorption equation was applied. The adsorption isotherms were studied at 30, 40, 50 and 60^0C. The plots of C_e/Q_e versus C_e at 30^oC for all the dyes were linear which indicate the applicability of the Langmuir adsorption isotherm and a representative plot is shown in figure 4. The statistical parameters were given in TABLE 3.

The essential characteristics of the Langmuir equation can be described by a dimensionless equilibrium parameter, R_L, which is defined as[11].

$$R_L=1/(1+bC_o) \quad (3)$$

Where b is the Langmuir constant(L mg^{-1}) and C_0 is the initial dye concentration(mgL^{-1}). The value of R_L indicates the shape of the isotherms to be either unfavorable($R_L>1$), linear($R_L=1$), favorable($0< R_L<1$) or irreversible($R_L=0$). The R_L values computed for the present system are provided in TABLE 4. The R_L values between 0 and 1 indicate favorable adsorption for all the initial concentrations and temperatures studied[7,12].

The adsorption data have been fitted to the freundlich isotherm. The linear plots of log Q_e ver-

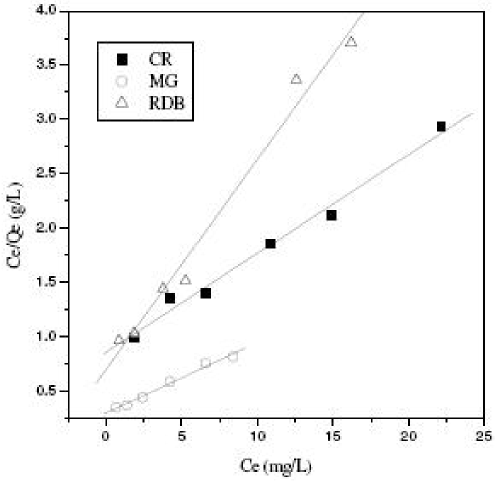

Figure 4 : Linear langmuir plot for the adsorption of dyes onto AMC

Temp=30°C ; pH=7

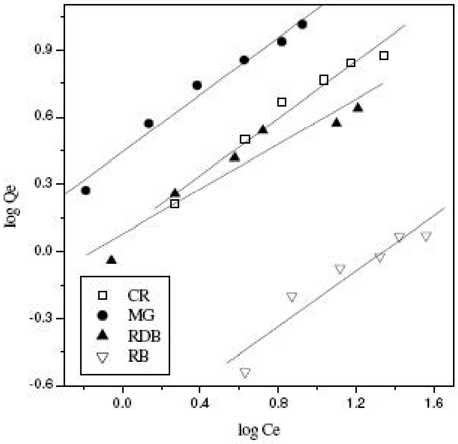

Figure 5 : Freundlich isotherms for the adsorption of dyes onto AMC

Temp=30°C ; pH=7

sus log C_e at different temperatures indicate the applicability of the Freundlich adsorption isotherm. A representative plot is shown in figure 5. The results (TABLE 5) indicate that the value of intensity of adsorption(n) is greater than unity signifies that the forces within the surface layer are attractive[13].

TABLE 3 : Langmuir isotherm results

Dye	Temp	Statistical parameters/constants			
	°C	r	sd	Q^0	b
Congo red	30	0.991	0.01	13.18	0.076
	40	0.989	0.02	13.51	0.077
	50	0.983	0.02	13.88	0.078
	60	0.978	0.03	14.03	0.081
Malachite green	30	0.997	0.01	13.89	0.258
	40	0.996	0.01	13.97	0.270
	50	0.995	0.01	14.25	0.277
	60	0.995	0.01	14.08	0.303
Rhodamine B	30	0.989	0.02	4.78	0.326
	40	0.992	0.01	4.78	0.348
	50	0.993	0.01	4.80	0.371
	60	0.995	0.01	4.74	0.423
Rose Bengal	30	0.971	0.03	1.65	0.078
	40	0.974	0.03	1.69	0.089
	50	0.977	0.03	1.80	0.096
	60	0.979	0.03	1.81	0.102

TABLE 4 : Equilibrium parameter, R_L

[Dye](mg L^{-1})	Temperature (°C)			
	30	40	50	60
Congo red adsorption				
10	0.568	0.564	0.561	0.552
20	0.396	0.393	0.390	0.381
30	0.304	0.303	0.299	0.291
40	0.247	0.245	0.242	0.235
50	0.208	0.206	0.204	0.198
60	0.179	0.177	0.176	0.170
Malachite green adsorption				
10	10	10	10	10
20	20	20	20	20
30	30	30	30	30
40	40	40	40	40
50	50	50	50	50
60	60	60	60	60
Rhodamine B adsorption				
10	10	10	10	10
20	20	20	20	20
30	30	30	30	30
40	40	40	40	40
50	50	50	50	50
60	60	60	60	60
Rose Bengal adsorption				
10	10	10	10	10
20	20	20	20	20
30	30	30	30	30
40	40	40	40	40
50	50	50	50	50
60	60	60	60	60

Thermodynamic parameters

The standard free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated from the variation of the thermodynamic equilibrium constant K_0. The values of K_0 for the adsorption process were determined by the reported method[14]. The thermodynamic parameters were calculated using the following equations.

$$\ln K^0 = (\Delta S^0/R) - (\Delta H^0/RT) \tag{4}$$

$$\Delta G^0 = -RT \ln K^o \tag{5}$$

ΔH^0 and ΔS^0 were determined from the slope

TABLE 5 : Freundlich isotherm results

Dye	Temp.	Statistical parameters/constants			
	^{0}C	r^2	sd	K	n
Congo red	30	0.992	0.02	2.03	1.41
	40	0.990	0.02	2.04	1.40
	50	0.988	0.03	2.05	1.39
	60	0.985	0.03	2.06	1.38
Malachite green	30	0.986	0.02	1.93	1.53
	40	0.985	0.02	1.93	1.52
	50	0.985	0.02	1.93	1.52
	60	0.984	0.03	1.92	1.53
Rhodamine B	30	0.950	0.05	1.72	1.85
	40	0.954	0.05	1.70	1.88
	50	0.959	0.04	1.68	1.92
	60	0.954	0.04	1.66	1.97
Rose Bengal	30	0.988	0.03	1.73	1.83
	40	0.992	0.01	1.77	1.75
	50	0.994	0.01	1.78	1.73
	60	0.995	0.01	1.78	1.72

TABLE 6 : Equilibrium parameters for the adsorption of dyes onto activated carbon

$[D]_0$	K_0				$-\Delta G^0$				ΔH^0	ΔS^0
	30^0	40^0	50^0	60^0	30^0	40^0	50^0	60^0		
Congo red adsorption										
10	4.33	4.44	4.56	4.68	3.69	3.88	4.08	4.28	2.06	18.9
20	3.69	3.87	4.07	4.38	3.29	3.52	3.77	4.09	3.79	23.4
30	3.57	3.80	4.05	4.33	3.20	3.47	3.76	4.06	4.99	27.0
40	2.69	2.83	2.98	3.13	2.50	2.71	2.93	3.16	4.01	21.5
50	2.35	2.46	2.57	2.70	2.15	2.33	2.54	2.74	3.61	18.9
60	1.71	1.78	1.81	1.88	1.35	1.50	1.59	1.75	2.24	11.8
Malachite green adsorption										
10	14.49	15.18	15.94	17.07	6.73	7.08	7.44	7.85	3.77	34.6
20	13.65	14.26	15.06	15.81	6.58	6.92	7.28	7.64	3.88	34.5
30	11.37	12.27	13.02	14.13	6.12	6.53	6.89	7.33	5.38	37.9
40	8.49	8.95	9.40	9.98	5.39	5.70	6.02	6.37	4.03	31.1
50	6.60	6.95	7.40	7.71	4.75	5.04	5.37	5.66	4.52	30.6
60	6.13	6.43	6.81	7.16	4.57	4.84	5.15	5.42	4.13	28.7
Rhodamine B adsorption										
10	10.38	11.19	12.12	13.47	5.89	6.28	6.69	7.19	6.15	39.6
20	9.75	10.47	10.95	12.58	5.74	6.11	6.43	7.01	4.62	34.2
30	6.94	7.32	8.00	8.54	4.58	5.18	5.58	5.93	5.60	34.5
40	6.60	6.65	6.86	7.17	4.75	4.93	5.17	5.45	1.58	20.6
50	2.97	3.09	3.23	3.34	2.74	2.94	3.15	3.33	3.35	20.0
60	2.70	2.81	2.93	3.04	2.50	2.69	2.89	3.08	3.26	19.0
Rose Bengal adsorption										
10	1.33	1.50	1.75	1.96	0.72	1.05	1.51	1.86	10.77	37.8
20	1.70	2.06	2.36	2.56	1.33	1.88	2.30	2.60	13.04	47.5
30	1.29	1.38	1.52	1.63	0.63	0.83	1.12	1.36	6.55	23.6
40	0.90	1.02	1.15	1.23	-0.26	0.05	0.37	0.58	9.71	31.1
50	0.89	0.98	1.08	1.15	-0.30	-0.04	0.20	0.38	7.85	24.9
60	0.65	0.73	0.83	0.90	-1.08	-0.80	-0.50	-0.27	9.65	28.2

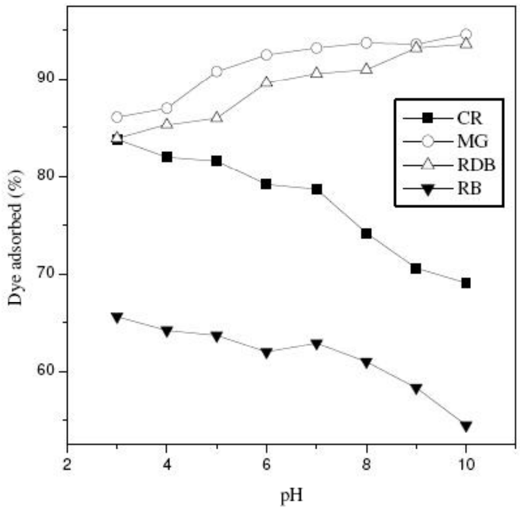

Figure 6 : Effect of initial pH on the adsorption of dyes onto AMC

[Dyes]=20mg/L; Temp=30^{0}C ; Contact time=60min

and intercept of the plot(not shown) of ln K_o versus 1/T.

The standard free energy change, enthalpy and entropy changes along with equilibrium constants were given in TABLE 6. The endothermic nature of adsorption is indicated by an increase in K_0 with rise in temperature. The negative values of ΔG^0 indicate that the reaction is spontaneous. The values of enthalpy of a sorption process may be used to distinguish between chemical and physical sorption[13-15]. For chemical sorption, enthalpy values range from 83 to 830kJmol^{-1}, while for physical sorption they range from 8 to 25kJmol^{-1}. On the basis of the above distinction, we conclude that the dyes sorption by AMC is a physical process. Positive values of ΔH^0 suggest that the process is endothermic, so an increase of temperature encourages dyes adsorption. Enhancement of adsorption capacity of AMC at higher temperatures may be attributed to the enlargement of the pore size and/or activation of the adsorbent surface and to the increase in the mobility of the dyes. As indicated in TABLE 6, ΔS^0 values for the adsorption process are positive. This observation suggests a high degree of disorderliness at the solid-solution interface during the adsorption of dyes onto AMC. This may be due to the fact that the adsorbed water molecules, which are 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[16].

Effect of pH

The influence of pH of the dye solution on the amount of dyes adsorbed was studied. The percent removal of dyes at different pH values is shown in figure 6. 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}=6.3). 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[17].

Kinetics of adsorption

Kinetics of sorption describes the solute uptake rate which in turn governs the residence time of sorption reaction. It must be remembered that the two important physico-chemical aspects for parameter evaluation of sorption process as unit operation are the kinetics and the equilibria. Hence in the present study, the kinetics of dyes removal has been carried out to understand the behavior of the adsorbent employed.

The sorption of dyes from liquid phase to solid phase can be considered as diffusion controlled first-order reversible process[12-18]. It can be expressed as:

$$A \underset{k_2}{\overset{k_1}{=}} B \tag{6}$$

Where k_1 is the forward rate constant and k_2 is the backward rate constant. A represents dye remaining in the solution and B represents dye retained on the surface of the adsorbent. If the first-order reversible kinetic model holds true, the rate equation for the reaction is expressed as:

$$\ln(1-X_A/X_{Ae})=k_{ad}\,t \tag{7}$$

The kinetic plots of $\ln(1-X_A/X_{Ae})$ versus t for different concentrations and temperatures were found to be linear with correlation coefficients greater than 0.95, indicating the applicability of first-order reversible kinetics. The forward(k_1) and backward(k_2) rate constants were calculated as described in the literature[19] and are summarized in TABLE 7. It is evident, from the results, that the forward rate constants are much higher than the backward rate constants suggesting that the rate of adsorption is clearly dominant. Further, the values of k_{ad} were found to increase with increase in the temperature indicating the endothermic nature of the adsorption process.

TABLE 7 : Rate constants for the adsorption of dyes (10^3K_{ad}, min^{-1}) and rate constants for the forward ($10^3 k_1$, min^{-1}) and reverse (10^3k_2,min^{-1}) processes

$[Dye]_0$	Temperature (^{0}C)											
	K_{ad}				30^0		40^0		50^0		60^0	
	30^0	40^0	50^0	60^0	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2
Congo red adsorption												
10	7.55	7.71	7.84	8.01	6.14	1.41	6.29	1.42	6.43	1.41	6.60	1.41
20	6.72	7.01	6.66	7.49	5.29	1.43	5.57	1.44	5.34	1.31	6.09	1.39
30	7.55	7.90	8.28	9.78	5.90	1.65	6.26	1.65	6.64	1.63	7.94	1.83
40	6.87	6.23	6.45	7.38	5.01	1.86	4.61	1.63	4.83	1.62	5.59	1.79
50	5.82	6.01	6.19	4.85	4.08	1.74	4.28	1.74	3.57	1.62	3.54	1.31
60	4.99	5.00	5.14	5.27	3.13	1.84	3.20	1.80	3.31	1.83	3.44	1.83
Malachite green adsorption												
10	10.02	10.42	10.83	11.45	9.38	0.64	9.78	0.64	10.19	0.64	10.82	0.63
20	7.88	8.50	8.83	9.58	7.34	0.54	7.95	0.56	8.28	0.55	9.01	0.57
30	8.65	9.22	9.42	10.12	7.95	0.70	8.53	0.69	8.75	0.67	9.45	0.67
40	7.72	8.33	8.40	9.09	6.91	0.81	7.49	0.83	7.59	0.81	8.27	0.83
50	6.13	6.71	6.26	7.30	5.32	0.81	5.87	0.84	5.52	0.75	6.47	0.84
60	5.82	6.40	6.60	6.90	5.00	0.82	5.54	0.86	5.75	0.84	6.05	0.85
Rhodamine B adsorption												
10	7.14	7.32	7.24	8.54	6.52	0.62	6.72	0.60	6.69	0.55	7.94	0.59
20	4.96	5.58	5.66	5.93	4.49	0.46	5.09	0.49	5.19	0.47	5.50	0.44
30	3.61	2.83	3.74	4.30	3.16	0.45	2.49	0.34	3.33	0.42	3.85	0.45
40	3.51	3.11	3.71	4.59	3.05	0.46	2.71	0.41	3.24	0.47	4.03	0.56
50	2.38	2.51	2.56	2.68	1.78	0.60	1.90	0.61	1.95	0.60	2.06	0.62
60	3.64	3.85	3.99	4.07	2.66	0.98	2.84	1.00	2.97	1.01	3.06	1.01
Rose Bengal adsorption												
10	6.64	7.08	7.72	8.25	3.80	2.84	4.24	2.83	4.92	2.80	5.46	2.79
20	5.97	7.27	7.55	7.89	3.76	2.21	4.89	2.38	5.30	2.25	5.68	2.22
30	8.53	6.77	7.08	7.54	4.79	2.73	3.93	2.84	4.27	2.81	4.68	2.86
40	5.61	5.94	6.27	6.34	2.66	2.95	3.00	2.94	3.78	2.49	3.50	2.84
50	5.46	5.71	6.06	6.16	2.57	2.90	2.83	2.88	3.15	2.91	3.30	2.86
60	5.01	5.06	4.58	5.07	1.97	3.04	2.14	2.91	2.08	2.51	2.41	2.66

The values of k_{ad} were found to decrease with increase in the initial concentration of dyes from 10 to 60 mg L^{-1}. An examination of the effect of dye concentration on the k_{ad} helps to describe the mechanism of removal taking place. In cases of strict surface adsorption, a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationships between initial solute concentration and the rate of reaction will not be linear. Hence, it seems likely that pore diffusion limits the overall rate of dye adsorption[20].

Intra-particle diffusion studies

In adsorption studies, it is necessary to determine the rate-determining step. Therefore, the results obtained from the experiments were used to study the rate-limiting step. Since the particles were

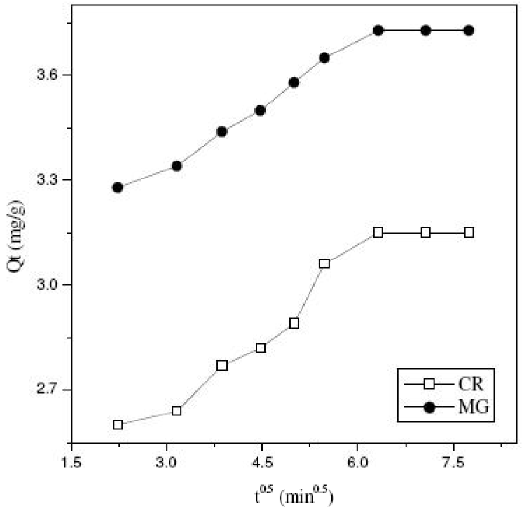

Figure 7 : Intraparticle diffusion curve for the adsorption of dyes onto AMC

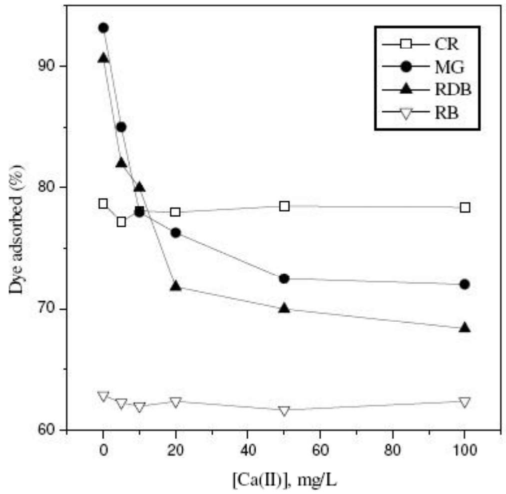

Figure 8 : Effect of addad calcium ions on the adsorption of dyes onto AMC

[Dyes]=20mg/L; Temp=30^0C ; pH=7; Contact time =60min

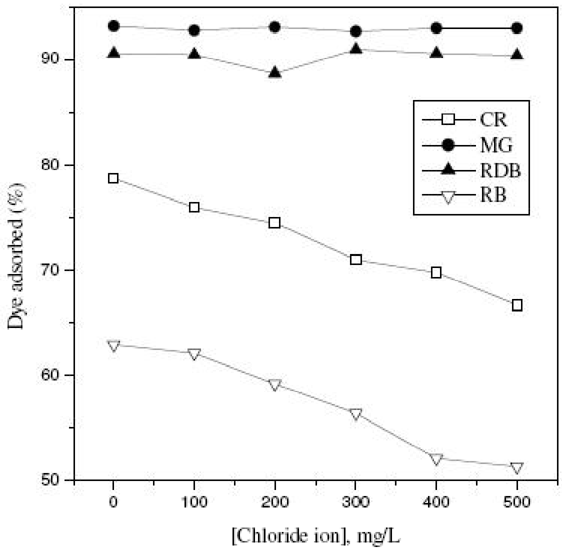

Figure 9 : Effect of addad chloride icon on the adsorption of dyes onto AMC

[Dyes]=20mg/L; Temp=30^0C ; pH=7; Contact time =60min

vigorously agitated during the experiment, it is reasonable to assume that the mass transfer from the bulk liquid to the particle external surface did not limit the rate. One might, then, postulate that the rate-limiting step might be film or intra-particle diffusion[21]. That is why, in this study, possibility of existence of intra-particle diffusion was tested by plotting the graph between amount of dye adsorbed and square root of time (Figure 7). The double nature of these plots may be explained as: the initial curve portions are attributed to boundary layer diffusion effect, while the final linear portions are due to intra-particle diffusion effect. The rate constant for intra-particle diffusion coefficient K_p, for the dyes was determined from slopes of linear portion of the respective plots. The values of K_p(in mg g^{-1} $min^{-0.5}$) are 0.109, 0.116, 0.053 and 0.024 for Congo red, Malachite green, Rhodamine B and Rose Bengal respectively. The amount of the dyes adsorbed (TABLE 2) was observed to be in the same order. The linear portions of the curves do not pass the origin in figure 7. This indicates that mechanism of dyes removal on the adsorbent is complex and both the surface adsorption as well as intra-particle diffusion contributes to the rate-determining step[22].

Effect of other ions

The effect of other ions like Ca^{2+} and Cl^- on the adsorption process was studied at different concentrations. The co-ions were added to 20 mg/L of dye solutions and the contents were agitated for 60min at 30^0C. The results (Figure 8-9) 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

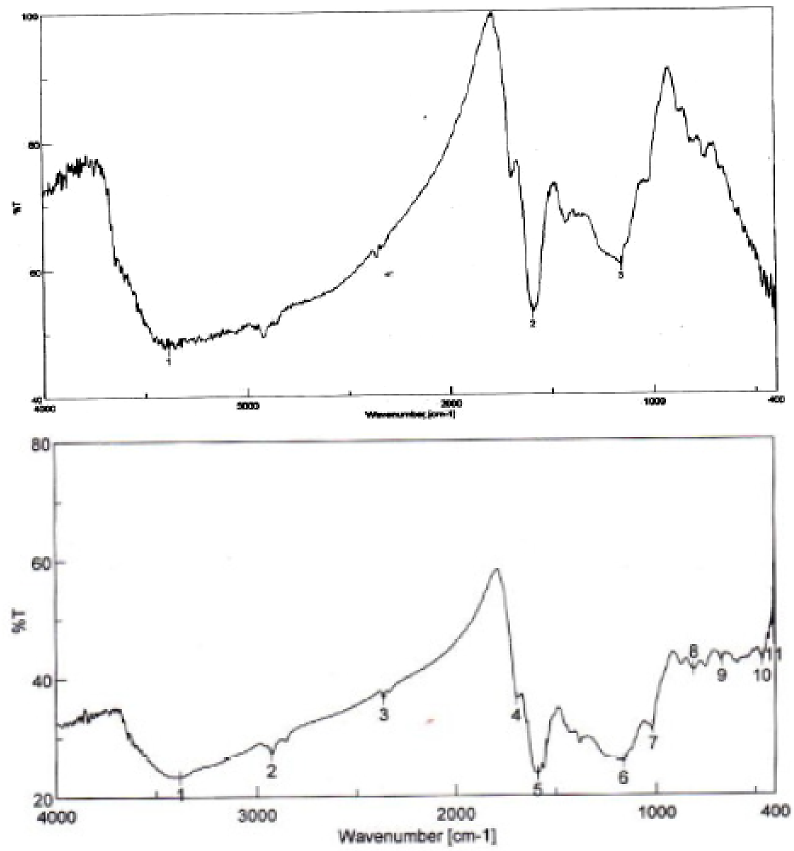

Figure 10 (a) : FT-IR spectrum of the adsorbent (AMC) before adsorption, (b) : FT-IR spectrum of the adsorbent after adsorption of Congo red

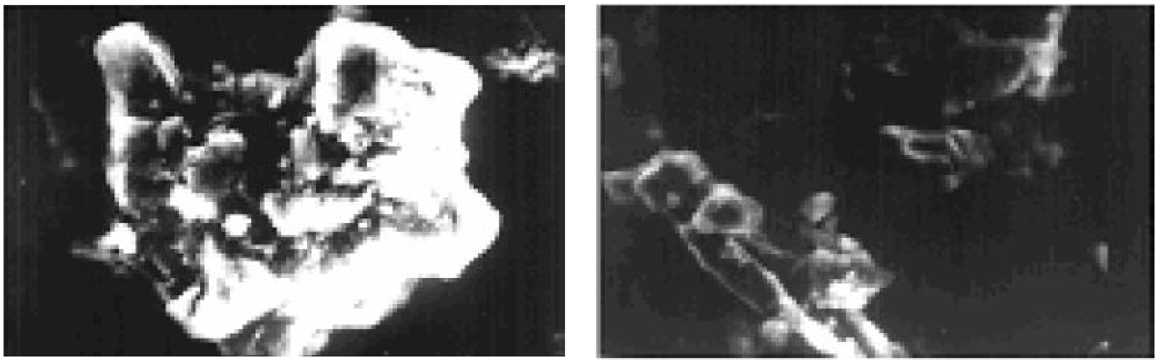

Figure 11 : SEM images of the adsorbent before adsorption (above) and after adsorption of Malachite green (below)

the presence of Ca^{2+} compared with Cl^- 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[23].

FT IR and SEM studies

The FT-IR spectra of the activated carbon before and after adsorption of dyes have been recorded and a representative spectrum is shown in figure 10. 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. The SEM images of raw activated carbon and dye-adsorbed activated carbon have been recorded and a representative image is given figure 11. The bright spots, shows the pres-

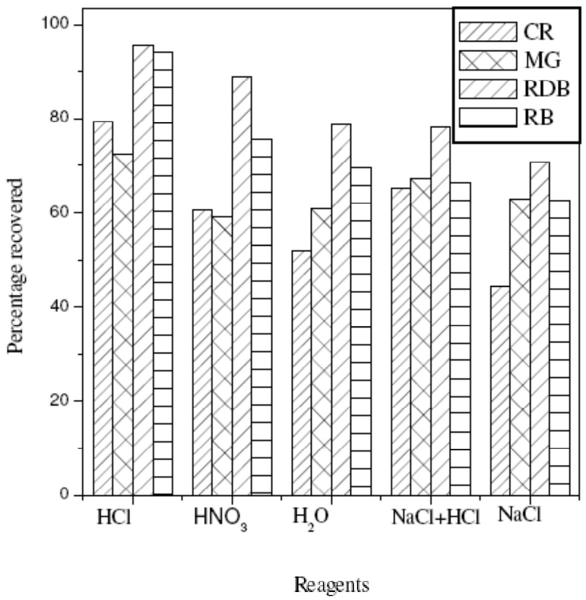

Figure 12 : Regeneration studies

ence 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[24].

Regeneration studies

A suitable method of desorption is needed for the recovery of dyes and regeneration of carbon. For this purpose different reagents(all 0.2 M) as extractant were tested. The results of the experiments are shown in figure 12. The relatively inexpensive HCl eluted maximum of the bound dyes from the carbon. In contrast HNO_3, water, NaCl, and NaCl + HCl were not those much efficient in the removal of dyes. An efficiency of over 75% was obtained by using 0.2 M HCl solution and is therefore suitable for the regeneration of the active carbon[25].

CONCLUSIONS

The experimental data obtained from equilibrium studies correlated reasonably well by the Langmuir and Freundlich adsorption isotherms and the isotherm parameters computed shed some light on the mechanism of adsorption process. The dimensionless separation factor, R_L, showed that the adsorption of dyes on to the activated carbon is favourable. The amount of dyes adsorbed depends largely on the initial pH of the medium and nature of the dye. The values of ΔH°, ΔS° and ΔG° results shows that the carbon employed has a considerable potential as an adsorbent for the removal of dyes. The mechanism of the adsorption process suggested by the results of kinetic and thermodynamic parameters is well supported by analytical measurements.

ACKNOWLEDGEMENT

S.Arivoli, Research Scholar under UGC, FDP scheme, thank the University Grants Commission, New Delhi, Director of Collegiate Education, Chennai and the Principal, M.R.Government Arts College, Mannargudi for permitting to carry out this research work successfully.

REFERENCES

[1] T.Robinson, G.McMullan, R.Marchant, P.Nigam; Biores.Technol., **77**, 247 **(2001)**.
[2] S.B.Wang, Y.Boyjob, A.Choucib, Z.H.Zh; Water.Res., **39**, 129 **(2005)**.
[3] Indra Deo Mall, Vimal Chandra Srivastava, Nitin Kumar Agarwal, Indra Mani; Colloids Surf. A.Physicochem Eng.Aspects, **264**, 17 **(2005)**.
[4] N.Kannan, A.Vanangamudi; Indian J.Environ Protect, **11**, 245 **(2005)**.
[5] Y.F.Xia, B.Xiao, K.M.Thomas; Langmuir, **18**, 470 **(2002)**.
[6] N.Muthulakshmi Andal; Studies on the Adsorption of Metal ions using Naturally occurring Polymers, Ph.D.Thesis, Gandhigram Rural University, Gandhigram, **(2003)**.
[7] K.Kadirvelu, C.Karthika, N.Vennilamani, S.Pattabhi; Chemosphere, **60**, 1009 **(2005)**.
[8] S.Senthilkumar, P.R.Varatharajan, K.Porkodi, C.V. Subburam; Colloid Inter.Sci., **284**, 79 **(2005)**.
[9] I.Langmuir; J.Amer.Chem.Soc., **40**, 1361 **(1918)**.
[10] H.Freundlich; Phys.Chemie., **57**, 384 **(1906)**.
[11] D.K.Singh, Bhavana Srivastava; Indian.J.Chem. Technol., **8**, 133 **(2001)**.
[12] V.Gopal, K.P.Elango; J.Hazardous Mat., **141**, 98 **(2007)**.
[13] V.Aravind, K.P.Elango; Indian J.Chem.Technol., **13**, 476 **(2006)**.
[14] K.Anoop Krishnan, T.S.Anirudhan; Indian J.Chem. Technol., **9**, 32 **(2002)**.
[15] B.Stephen Inbaraj, N.Sulochana; Indian J.Chem.

Technol., **9**, 201 **(2002)**.

[16] A.Ramesh, D.J.Lee, J.W.C.Wong; J.Colloid Interface Sci., **291**, 588 **(2005)**.

[17] S.S.Tahir, Rauf Naseem; Chemosphere, **63**, 1842 **(2006)**.

[18] S.Rengaraj, R.Sivabalan, Banumathi Arabindoo, V.Murugesan; Indian J.Chem.Technol, **7**, 127 **(2000)**.

[19] K.Vasanthakumar, V.Ramamurthi, S.Sivanesan; Dyes and Pigments, **69**, 102 **(2006)**.

[20] S.D.Khattri, M.K.Singh; Indian J.Chem.Technol, **3**, 114 **(1999)**.

[21] Mohammad Badruzzaman, Paul Westerhoff, R.U. Detlef Knappe; Water.Res., **38**, 4002 **(2005)**.

[22] Krishna G Bhattacharyya, Arunima Sharma; J. Environ Manage., **71**, 217 **(2004)**.

[23] T.G.Chuah, A.Jumasiah, I.Azni, S.Katayon, S.Y. Thomas Choong; Desalination, **175**, 305 **(2005)**.

[24] S.Venkata Mohan, S.Krishna Mohan, J.Karthikeyan; J.Sci.Indust.Res., **60**, 410 **(2000)**.

[25] G.N.Manju, C.Raji, T.S.Anirudhan; Water.Res., **32**, 3062 **(1998)**.