Biosorption of malachite green dye in aqueous solution using the acid activated *Cynodon dactylon* (L.) Pers. Bark Carbon (CBC)

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Abstract

Legislation about toxic substances in industrial waste waters is becoming increasingly strict. Consequently, a large number of researches are addressing the variety of issues in this area. Dyes are common constituents of effluents discharged by various industries. The present study was undertaken to find out a suitable low cost, environmental friendly and highly effective bio-sorbent to remove malachite green from aqueous solution. The effect of temperature on the equilibrium adsorption of dye from carbon was investigated. The equilibrium adsorption data was analysed using two widely applied isotherms, namely, Langmuir and Freundlich isotherms. A non-linear method was used for comparing the best fit of the isotherm. Both the isotherms were found to be fit. Thermodynamic parameters such as $\Delta G°$, calculated using $\Delta H°$ and $\Delta S°$, were calculated using adsorption equilibrium constant obtained from the Langmuir isotherm. From kinetic reversible First order kinetics were studied. Results suggested that the malachite green adsorption on CBC was a spontaneous and endothermic process.

Keywords: Acid activated *Cynodon dactylon* bark carbon (CBC), Adsorption isotherm, Equilibrium, Intra particle diffusion, Kinetic and Thermodynamic parameters, malachite green, Regeneration pattern

INTRODUCTION

A safe potable drinking water is necessary for every human being. Due to over population, India is suffering from persistent demand of safe drinking water. Dye and dye intermediates industries are the largest sector of chemical industries in India, since they are used in textile, paints, pulp and paper industries. More than 80% of their production is utilized by the textile industries. A huge amount of water is necessary by these industries for the cleaning and washing purposes and they discharge highly colored effluents containing different dyes. These highly colored effluents upsets the biological processes in aquatic environments and they are even carcinogenic. Unless, properly collected, treated and disposed of, such type of waste waters create serious water pollution problems. Some dyes can cause allergic dermatitis, skin irritation, cancer and mutation in man. As per recent estimates approximately 12% of synthetic textile dyes used each year is being lost during manufacture and processing operations and 20% of these dyes enter the environment through effluents that result from the treatment of residual industrial wastes. 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 (Weber and Stickney, 1993). Waste waters from dyeing industries are 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 color removal and it has certain disadvantages. Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed due to its high adsorption capacity (Uzun *et al.*, 2000; Sudha *et al.*, 2007 and Vasu, 2008). To minimize the ill effects caused by the contaminated water, the concentration and effective utilization of activated carbon generated from natural plant materials have attracted worldwide attention. Different cheap adsorbents are used or under investigations. For eg., peat, marine algae, clays, maize cob, bagase, palm fruit bunch, lalang leaf, *Saraca indica* leaf and nile rese plant, could be to remove dyes and metal ions from waste water (Nassar *et al.*, 1997; Qiming *et al.*, 1999; Ho and Mckay, 2000; Nassar *et al.*, 2004; Hanafiah *et al.*, 2006; Abdel Ghani and Elchaghaby, 2007 and Goyal *et al.*, 2008). Besides that many chelating polymers could also be used for this purpose (Samal *et al.*, 2001; Coskun and Soyakan, 2006; Masram *et al.*, 2007 and Yigitoglu and Arslan, 2007). The cell wall of most agricultural wastes contain natural polymers like cellulose, hemi cellulose, pectin and lignin which are the most important sorption sites (Qaiser *et al.*, 2007). The present study was undertaken to evaluate the efficacy of a carbon adsorbent prepared from acid activated *Cynodon dactylon* bark

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carbon (CBC) for removal of malachite green dye in aqueous solution. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer processes is essential. In this paper, we have reported the applicability of kinetic and mass transfer models for the adsorption of malachite green by acid activated CBC.

MATERIALS

Preparation of Acid Activated *Cynodon dactylon* bark Carbon (CBC)

The dried *Cynodon dactylon* was carbonized with concentrated sulphuric acid in the weight ratio of 1:1(W/V). Heating for twelve hours in a furnace at 600°C has completed the carbonization and activation. 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 125°C in a hot air oven. The dried material was ground well to a fine powder and sieved.

Batch Adsorption Studies

Batch adsorption experiments were conducted by adding known weight of adsorbent material to 50 ml of the dye solution with concentrations of 15, 30, 45, 60, 75 mg/l at various temperatures of 35, 45, 55, and 65°C. The flasks were shaken vigorously using a mechanical shaker rotating with a speed of 125 rpm. The solution was then filtered through Whatman filter paper (No, 42) at preset time intervals (10 minutes) and the residual dye concentration was measured. The per cent adsorption (%) and distribution ratio (K_d) were calculated using the equation.

$$\% \text{ Adsorption} = C_i - C_r / C_r \times 100 \text{ ————[1]}$$

Where C_i and C_r are the concentrations of the metal ion in initial and final solutions, respectively, and

$$K_d = \text{amount of metal in adsorbent} / \text{amount of metal in solution} \times V/m \text{ ml/g ——[2]}$$

Where V is the volume of the solution (ml) and m is the weight of the adsorbent (g). The percent adsorption and K_d (ml/g) can be correlated by the following equation (Khan et al., 1995).

$$\% \text{ Adsorption} = 100 K_d / K_d + V/m \text{ ————[3]}$$

Effects of Variable parameters

Effect of adsorbent and initial concentration of adsorbate

The different doses of the adsorbents were mixed with the different initial concentrations of dyes ranging from 15, 30, 45, 60, 75 mg/l and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses and rate of adsorption were determined at definite time intervals by keeping all other factors constant.

Effect of Contact time and pH

The effect of period of contact on the removal of the dye on adsorbent in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and concentration of other ions constant. Adsorption experiments were carried out at pH 3 to 9. The pH of the samples were determined using a portable pH meter of Systronics make. The pH meter was calibrated with 4.0 and 9.2 buffers. The acidic and alkaline pH of the medium was maintained by adding the required amounts of dilute hydrochloric acid or sodium hydroxide solutions. While carrying out the experiments all other factors were kept constant.

Effect of Chloride ion

Using various sodium chloride solutions, the experiments were done in the presence of varying chloride environments.

Effect of Temperature

The experiments were carried out in 4 different temperatures viz. 35, 45, 55 and 65°C in a thermostat attached with a shaker of Remi make. The accuracy was maintained at ±0.5°C.

Zero point charge

The pH drift method (Jia and Thomas, 2002) was used to measure the pH at the potential of zero charge of the carbon (pH_{zpc}). 0.01M sodium hydroxide or hydrochloric acid was used to adjust the pH of the solution. Dissolved carbon di oxide was removed at 25°C when nitrogen was bubbled through the solution. 50mg of the activated CBC was added to 50ml of the dye solution. The final pH was recorded after stabilization. The zero point charge of the activated CBC was determined by plotting the graph between final pH versus initial pH values.

Neutralization studies

As per Boehm (Jia and Thomas, 2002), sodium carbonate was used to neutralize the strong acidic carboxylic acid groups like lactones, lactol and carboxyl group and sodium hydroxide was used to neutralize surface basic groups like pyrones and chromenes. Pi electron system of carbon basal planes have been used to describe the basic properties to surface basic groups. The results indicated that the activated CBC used might possess acidic oxygen functional group on their respective zero point charge values. The results obtained from the above neutralization studies are given in Table 1.

Regeneration studies

Regeneration studies were used to identify the nature of adsorption and recycling of the spent CBC and the malachite green dye. The effect of 0.2 M mineral acids and sodium chloride solutions were taken for the regeneration of the adsorbed carbon.

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Analytical Measurements

The FT – IR, SEM images and XRD patterns of the adsorbents before and after adsorption were recorded at the CECRI, Karaikudi, South India.

RESULTS AND DISCUSSION

Sorption activity of the adsorbent

The chemical nature and pore structure usually determine the sorption activity. The wide usefulness of carbon is a result of their specific surface area, high chemical and mechanical stability. The chemical composition of the chosen CBC adsorbent are listed in the following Table 1.

Effect of Adsorbent Dosage

The amount of adsorbent employed was found to influence the efficiency of the adsorption process. This parameter was optimized in conjuction with the other optimized parameters (10 – 100 mg/50 ml) for 45 mg/l of malachite green removal increases with increasing

Table 1. Chemical composition of the CBC adsorbent

| Properties	CBC
Particle size (mm)	0.025
Density (g/cc)	0.1528
Moisture content (%)	0.98
Loss on ignition (%)	82
Acid insoluble matter (%)	3.2
Water soluble matter (%)	0.39
pH of aqueous solution	6.3
pH $_{zpc}$	5.4
Surface groups (m equiv/g)	
(i) Carboxylic acid	0.325
(ii) Lactone, lactol	0.074
(iii) Phenolic	0.067
(iv) Basic (pyrones and chromenes)	0.026

the CBC concentration (Figure 1). This could be attributed to increased CBC surface area and availability of more adsorption sites (Namasivayam and Yamuna, 1995; Namasivayam *et al.*, 1996). Hence the entire study was carried out with the adsorbent dose of 25 mg of adsorbent/50 ml of the adsorbate solution.

Effect of Agitation Time

The effects of agitation time on the amount of dye on adsorbent surface area is shown in Table 2 and Figure 2. Equilibrium was established at 60 minutes. Figure 2 revealed that the curve are smooth and continuous, leading to saturation, suggesting the possible monolayer coverage of the dye on CBC surface (Sudha *et al.*, 2007). Once again there is not a big change of amount of metal ion adsorbed with time, which gives an indication of ion exchange mechanism.

Effect of Initial malachite green dye concentration

A series of experiments were performed at different initial dye concentration *viz.*, (15, 30, 45, 60 and 75 mg/l) and time interval of 10 minutes up to 90 minutes at a temperature of 35°C and pH 5.4 (Figure 2 and
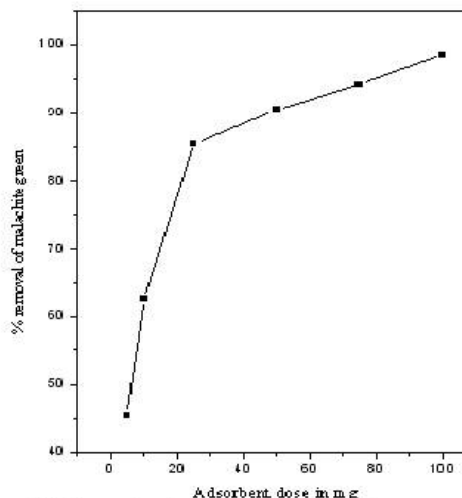
Figure 1. Effect of adsorbent dose on the removal of malachite green by CBC
[MG] = 45 mg/l; Contact time=60 minutes; Temperature = 35°C
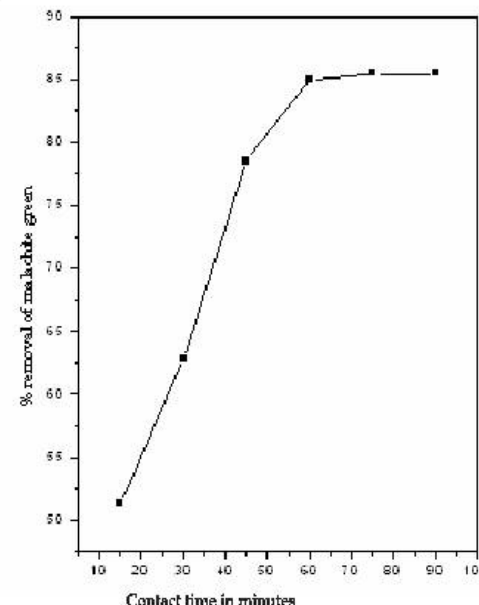
Figure 2. Effect of contact time on the removal of malachite green by CBC

Table 2). The values revealed that, per cent adsorption decreased with increase in initial dye concentration; but the actual amount of dye adsorbed per unit mass of carbon increases with increase in dye concentration. From this, we know that the adsorption is highly dependent on initial concentration of dye. It is because of that at lower concentrations, the ratio of the initial number of dye molecules to the available surface area is low and subsequently the practical adsorption becomes

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Table 2. Equilibrium parameters for the adsorption of malachite green by activated carbon (CBC)

Malachite green concentration (mg/l)	C_e (mg/l)				Q_e (mg/g)				Dye removed (%)			
	35°C	45°C	55°C	65°C	35°C	45°C	55°C	65°C	35°C	45°C	55°C	65°C
15	1.5241	1.2598	1.0128	0.7832	26.9518	27.4804	27.9744	28.4336	89.84	91.60	93.24	94.77
30	3.8972	3.5888	3.1020	2.6534	52.2056	52.8224	53.7960	54.6932	87.00	88.03	89.66	91.15
45	6.5433	5.7945	5.0921	4.2836	79.9134	78.4110	79.8158	81.4328	85.45	87.12	88.68	90.48
60	13.5428	12.6934	11.7144	10.6928	92.9144	94.6132	96.5752	98.6144	77.42	78.84	80.47	82.17
75	21.6534	19.9899	18.5629	17.0285	106.6932	110.0202	112.8742	115.9430	71.11	73.34	75.24	77.29

independent of initial concentration. The percentage removal of dye has been reported to be dependent upon initial concentration by earlier research also (Namasivayam and Yamuna, 1995: Namasivayam *et al.*, 1996).
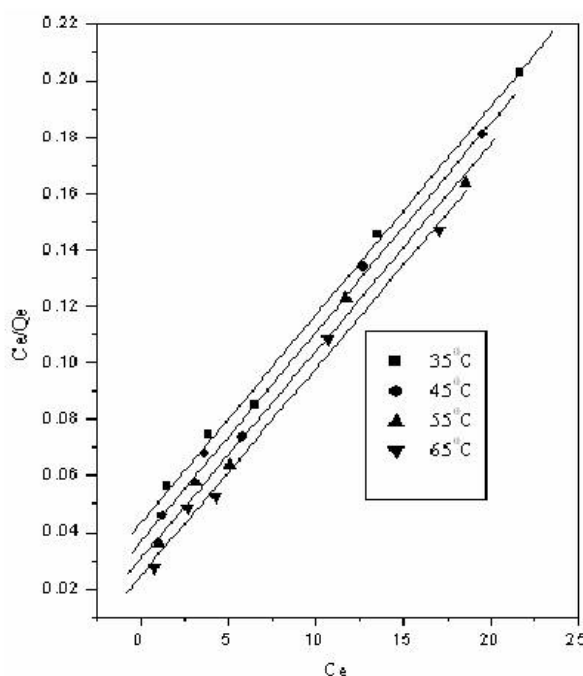
Adsorption Isotherm

The adsorption isotherms are important to describe how adsorbates will interact with adsorbents and so are critical for design purpose. Therefore, the correlation of equilibrium data using an equation is essential for evaluating practical adsorption (Hashem *et al.*, 2007). The adsorption isotherm was used to characterize the equilibrium between the amount of adsorbate that accumulated on the adsorbent and the concentration of the dissolved adsorbate. In this study, the experimental isotherm data set obtained was fitted using adsorption models including the Langmuir and Freundlich isotherms.

The Langmuir adsorption isotherm and the Freundlich isotherm are two common isotherms used to describe equilibria (Domenico and Schwartz, 1990; Reddi and Inyang, 2001; Nitzsche ans Vereecken, 2002 and Badmus *et al.*, 2007). The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbent and it represents the equilibrium distribution of dye and CBC adsorbent. The basic assumption of the Langmuir adsorption process is the formation of a monolayer of adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place.

The Langmuir isotherm has been represented by the following equation (Arivoli *et al.*, 2007).

$$C_e/Q_e = 1/Q_m b + C_e/Q_m \text{————————[4]}$$

C_e is the equilibrium concentration of adsorbate (mg/l), Q_e is the amount adsorbed at equilibrium (mg/g) and Q_m and b is Langmuir constants related to adsorption efficiency and energy of adsorption efficiency and energy of adsorption, respectively. The linear plots of C_e/Q_e

Figure 3. Linear Langmuir isotherm for the adsorption of malachite green

versus C_e suggest the applicability of the Langmuir isotherms. (Figure3). Values of Q_m and b were determined from slope and intercepts of the plots and are presented in Table 3. From the results, it is clear that the value of

Table 3. Langmuir isotherm results for the adsorption of malachite green (CBC)

Temperature (°C)	Statistical parameters/constants		
	r^2	Q_m	b
35	0.9979	135.70	0.1696
45	0.9970	137.17	0.1945
55	0.9828	145.04	0.1829
65	0.9961	136.29	0.2967

absorption efficiency Q_m and adsorption energy b of the CBC increases on increasing the temperature. From this, we can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. The Freundlich adsorption isotherm is an indication of the extent of heterogeneity of the adsorbent surface, Freundlich model is generally found to be better suited for characterizing multi – layer adsorption process. The Freundlich isotherm was represented by

$$\log Q_e = \log Kf + \frac{1}{n}\log C_e \quad ----------[5]$$

Where Q_e is the amount of malachite green dye adsorbed (mg/g), C_e is the equilibrium concentration of dye in solution (mg/l) and Kf and n are constants
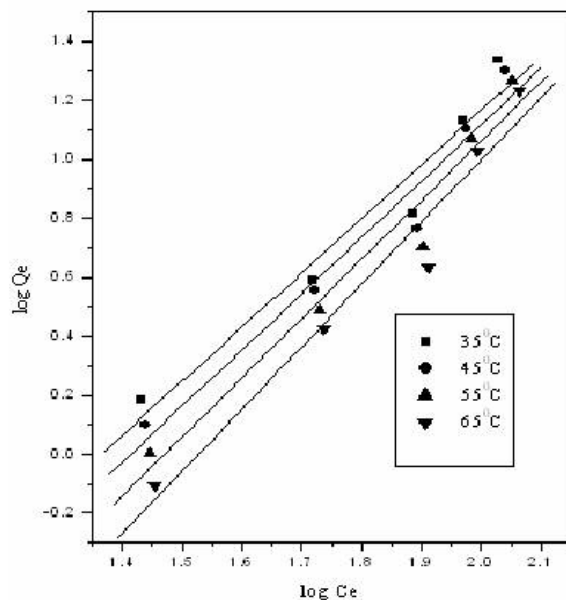

Figure 4. Linear Freundlich isotherm for the adsorption of malachite green

incorporating the factors affecting the adsorption capacity and intensity of adsorption respectively. Linear plots of log Q_e versus C_e showed that the adsorption of malachite green dye obeys Freundlich isotherm Figure 4. The values of Kf and n are given in the Table 5 which showed that the increase in negative charges on the adsorbent surface that makes electrostatic force like Vanderwaals between the CBC carbon surface and dye. The values of n which are greater than one indicated the adsorption was much more favorable (Arivoli *et al.*, 2007). The intensity of adsorption is an indicative of the bond energies between dye and adsorbent and the possibility of slight chemisorptions rather than physisorption (Arivoli *et al.*, 2005; Arivoli and Hema, 2007). The Freundlich type behavior is

indicative of the surface heterogeneity of the adsorbents, i.e, the adsorptive sites (surface of activated carbon) are made up of small heterogeneous particles in themselves. The activation of adsorption sites takes place, leading to increased adsorption probably through the surface exchange mechanism. The high values of r^2 (> 95%) for both isotherms showed that the adsorption of malachite

Table 4. Dimensionless separation factor (R_L) for the adsorption of malachite green (CBC)

Malachite green concentration mg/l	Temperature (°C)			
	35	45	55	65
15	0.282	0.255	0.268	0.183
30	0.164	0.146	0.154	0.101
45	0.116	0.102	0.108	0.069
60	0.089	0.079	0.083	0.053
75	0.073	0.064	0.068	0.043

Table 5. Freundlich isotherm results for the adsorption of malachite green (CBC)

Temperature (°C)	Statistical parameters/constants		
	r^2	K_f	n
35	0.9743	1.6763	1.9356
45	0.9776	1.6507	1.9950
55	0.9792	1.6136	2.0899
65	0.9799	1.5764	2.1968

green could be well described by both the Langmuir and Freundlich isotherms (Table 3 and 5). The value of R_L, calculated from the above expression and has been given in Table 4 lied in the range of 0.282 to 0.043, which indicated favorable adsorption of malachite green oxalate on *Cynodon dactylon* Carbon (CBC) for all studied concentrations at 308, 313, 318 and 323 K.

Kinetic studies

First order reversible model

The sorption of malachite green from adsorbent may be considered as a reversible reaction with an equilibrium state being established between two phases. A simple first order reaction model was therefore, used to correlate the rates of reaction which can be expressed as given by (Hamadi *et al.*, 2001).

$$\ln[1 - U_{(t)}] = K^n t \quad ----------[6]$$

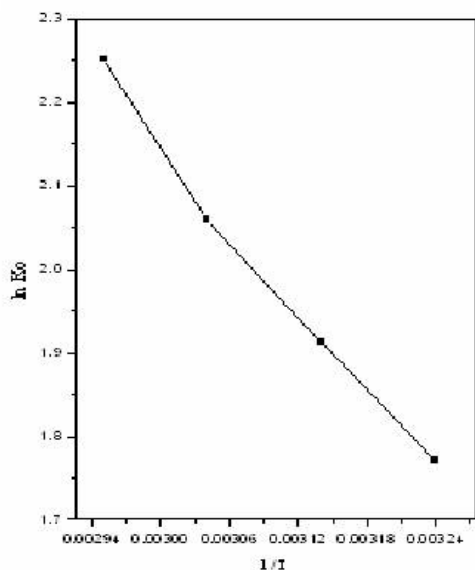Where K^n is the overall rate constant and calculated by following equation

$$K^n = K_t(1 + 1/K_c) + K_1 + k_2 \quad ------[7]$$

and K_1 and k_2 and K_c can be obtained from

$$K_c = K_1/K_2 = C_{Ae}/C_e \quad ------------[8]$$

$$U(l) = X/X_e \quad \text{————————————} \quad [9]$$

Where U(l) is called the fractional attainment of equilibrium. Therefore a plot of $-\ln(1 - U(l))$ versus time (min) will give a straight line. Constants K_1, K_2, K^n

Figure 5. Vant Hoff's plot for the adsorption of malachite green by CBC
[MG]=45mg/l; Adsorbent dose =25mg/50ml; Contact time = 60minutes.

and Kc were calculated using Eqn (7) and (8) (Hasan *et al.*, 2005).

In order to analyse the biosorption kinetics of dye, the first order kinetic model was applied to the experimental
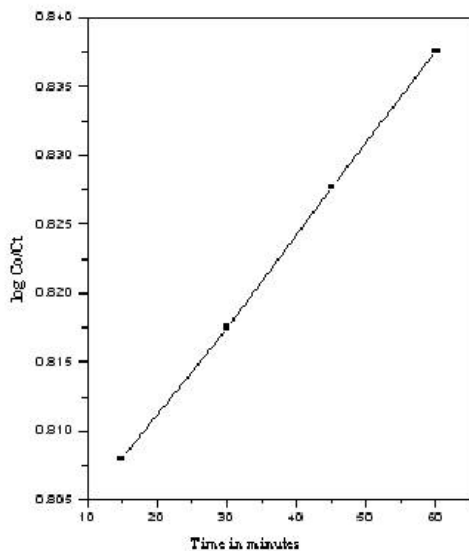
Figure 6. Natarajan - Khalaf plot for the adsorption of malachite green by CBC
[MG]=45mg/l; Adsorbent dose =25mg/50ml; Contact time = 60minutes, Temperature = 35°C

data. The first order rate expression of Lagergren can be expressed as (Lagergren *et al.*, 1898).

$$\log(q_e - q_t) = Kt/2.303 + \log q_e \quad \text{————————} [10]$$

Where q_e and q_t are the amount (g g^{-1}) of dye adsorbed at equilibrium and at time 't' respectively and K is the overall rate constant. Straight lines were obtained by plotting $\log(q_e \cdot q_t)$ against t, as shown in Figure 6. This indicated that dye sorption by CBC follows the first order kinetics (Table 6 and Table 7).

Table 6. Rate constants for the adsorption of malachite green dye ($10^3 k_{ad}$, min^{-1})

Malachite green concentration mg/l	k_{ad} Temperature (°C)			
	35	45	55	65
15	10.11	12.02	13.12	14.42
30	8.04	8.67	9.35	10.05
45	6.77	7.58	8.49	9.27
60	4.74	5.08	5.37	5.71
75	4.46	4.79	4.94	5.33

Effect of temperature

The adsorption capacity of the carbon increased with increase in the temperature of the system from 35°-65°C. Thermodynamic parameters such as change in free energy ($\Delta G°$) (kJ/mol), enthalpy ($\Delta H°$) (kJ/mol) and entropy ($\Delta S°$) (J/K/mol) were determined using the following equations

$$K_0 = C_{solid}/C_{liquid} \quad \text{————————————} [11]$$

$$\Delta G° = -RT \ln K_0 \quad \text{————————————} [12]$$

$$\log K_0 = \Delta S° / (2.303RT) - \Delta H°/(2.303RT) \quad \text{————} [13]$$

Where Ko is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin and R is the gas constant. The $\Delta H°$ and $\Delta S°$ values obtained from the slope and intercept of Vant Hoff's plots (representative Fig. 5) have presented in Table 8.

The values of $\Delta H°$, $\Delta S°$ and $\Delta G°$ were calculated as previously. Positive values of $\Delta H°$ and $\Delta S°$ suggested endothermic reaction, while the negative values of free energy change ($\Delta G°$) indicated that the adsorption was spontaneous (Table 6). The positive values of $\Delta S°$ suggested the increased randomness at the solid-solution interface during desorption of malachite green oxalate on *Cynodon dactylon* carbon. In desorption of the dye, the adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions, thus allowing for the prevalence of randomness in the system (Renmin Gong *et al.*, 2005; Sudha *et al.*, 2007).

Table 7. Rate constants for the adsorption of malachite green dye (10^3 k_{ad}, min^{-1}) by CBC and the constants for forward (10^3 k_1, min^{-1}) and reverse (10^3 k_2, min^{-1}) processes at various temperatures.

Malachite green concentration (mg/l)	Temperature (°C)							
	35°		45°		55°		65°	
	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2
15	9.09	1.02	11.01	1.01	12.24	0.88	13.67	0.75
30	7.00	1.04	7.64	1.03	8.38	0.97	9.16	0.89
45	5.79	0.98	6.61	0.97	7.53	0.96	8.39	0.88
60	3.68	1.06	4.01	1.07	4.33	1.04	4.70	1.01
75	3.18	1.28	3.52	1.27	3.72	1.22	4.12	1.21

Intraparticle diffusion

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intraparticle diffusion plot. Previous studies by various researchers showed that the plot of Qt versus $t^{0.5}$ represents multi linearity, which characterizes the two or more steps involved in the sorption process. According to Weber and Morris, (1962)
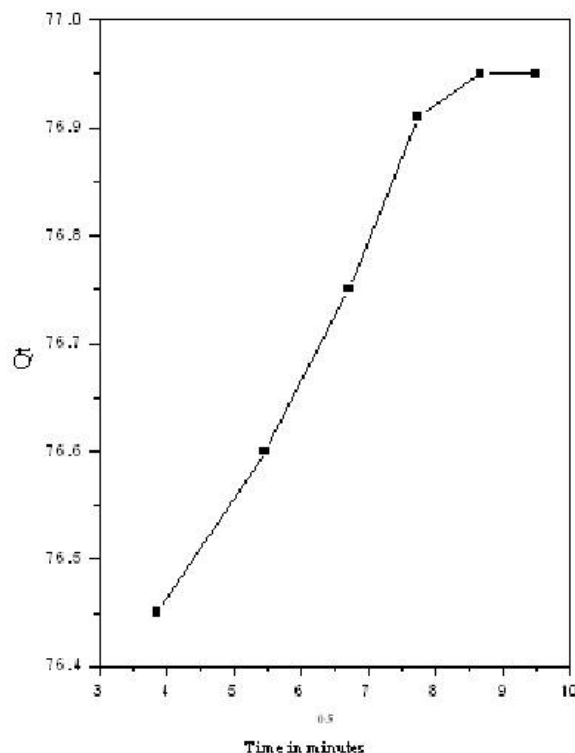
Figure 7. Intra-particle diffusion effect for the adsorption of malachite green by CBC
[MG]=45mg/l; Adsorbent dose =25mg/50ml; Contact time = 60minutes, Temperature = 35°C

an intraparticle diffusion coefficient K_p is defined by the equation:

$$K_p = Q/t^{0.5} + C \quad\quad\quad [14]$$

Thus the K_p (mg/g min$^{0.5}$) value can be obtained from the slope of the plot of Qt(mg/g) versus $t^{0.5}$ for malachite green. From figure 7, it was noted that the sorption process tends to be followed by two phases. The two phases in the intraparticle diffusion plot suggested that the sorption process proceeds by surface sorption and intraparticle diffusion (Weber *et al.,* 1967 and Vadivelan and Vasanthakumar, 2005;). The initial curved portion of the plot indicates a boundary layer effect while the second linear portion is due to intraparticle or pore diffusion. The slope of the second linear portion of the plot has been defined as the intraparticle diffusion parameter K_p (mg/g min$^{0.5}$). On the other hand, the intercept of the plot reflects the boundary layer effect. The larger the intercept the greater would be the contribution of the surface sorption in the rate limiting step. The calculated intraparticle diffusion coefficient K_p values were 0.042, 0.072, 0.099, 0.125 and 0.167 mg/g min$^{0.5}$ for initial dye concentrations of 15,30,45,60 and 75 mg/l, respectively, at 35°C.
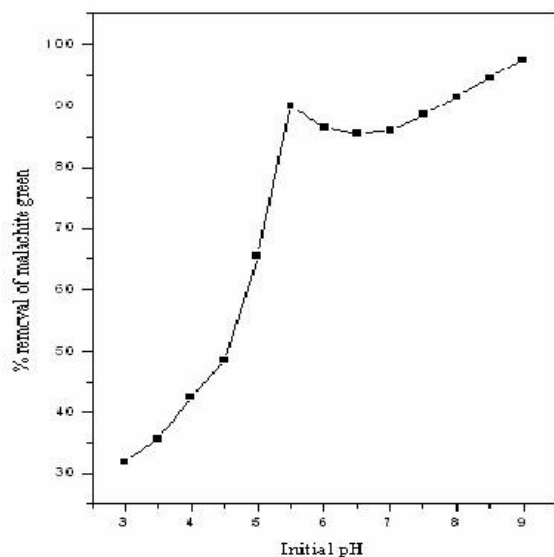
Effect of pH

The influence of pH on the dye adsorption by activated carbon (CBC) was studied while the dye concentration, shaking time and amount of adsorbent were fixed. The variation of malachite green adsorption on CBC over a pH range of 3 - 9 is shown in Fig.8. The results revealed that the adsorption of the dye increased from 34 to 90% with an increase in pH of the solution from 3 to 9 and then remains almost constant. The adsorption of these charged dye groups by the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which is in turn influenced by the solution pH. The pHzpc value for CBC was 5.4. At pH values

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Table 8. Equilibrium constant and thermodynamic parameters for the adsorption of malachite green by activated carbon (CBC).
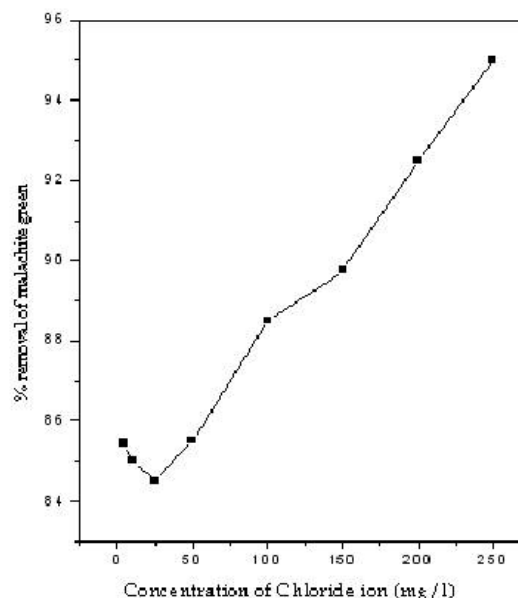
Malachite green concentration (mg/l)	K_0				ΔG^0				ΔH^0	ΔS^0
	Temperature (°C)									
	35°	45°	55°	65°	35°	45°	55°	65°		
15	8.84	10.91	13.81	18.15	-5.52	-6.32	-7.16	-8.15	20.47	84.30
30	6.69	7.35	8.67	10.31	-4.82	-5.28	-5.89	-6.55	12.45	55.94
45	5.87	6.76	7.83	9.51	-4.49	-5.05	-5.61	-6.33	13.58	58.63
60	3.43	3.72	4.12	4.61	-3.13	-3.48	-3.86	-4.30	8.45	37.55
75	2.46	2.75	3.04	3.40	-2.29	-2.67	-3.04	-3.44	9.16	37.16

below pHzpc the adsorbent had net positive charge and would, therefore, be prone to electro statically repel cations. Malachite green is a cationic basic dye as denoted by the presence of the positive nitrogen ion in its structure. On dissolution, the oxalate ion enters the aqueous solution ensuring that the dye has an overall positive charge. The positive charge on the cationic dye should ensure that it is attracted by an anionic adsorbent.

In carbon–aqueous systems the potential of the surface is determined by the activity of ions (e.g. H^+ and pH), which react with the carbon surface. For the carbon surface the potential determining ions are H^+ and OH^- and complex ions formed by bonding with H^+ and OH^-. The broken bonds along the surface of the carbon result in hydrolysis.

Figure 9. Effect of chloride ion on the removal of malachite green by CBC
[MG]=45mg/l; Adsorbent dose =25mg/50ml; Contact time = 60minutes, Temperature = 35°C

At low pH the reaction might be:

$$CBC\text{-}OH + H^+ \rightarrow CBC\text{-}OH^+_2$$
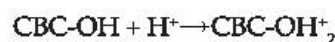
At high pH the reaction is:

$$CBC\text{-}OH + OH^- \rightarrow CBC\text{-}O^- + H_2O$$

In the present study, the adsorption is maximum at pH 9. So, it is identified that, at high pH, the solution in contact with the basal oxygen surface of the tetrahedral sheet will contain excess hydroxyls and the surface will then exhibit a cation exchange capacity (Sreedhar and Anirudhan, 1999; Yupeng Guo *et al.*, 2005 and Tahir and Naseem Rauf, 2006).
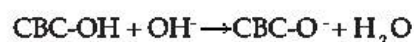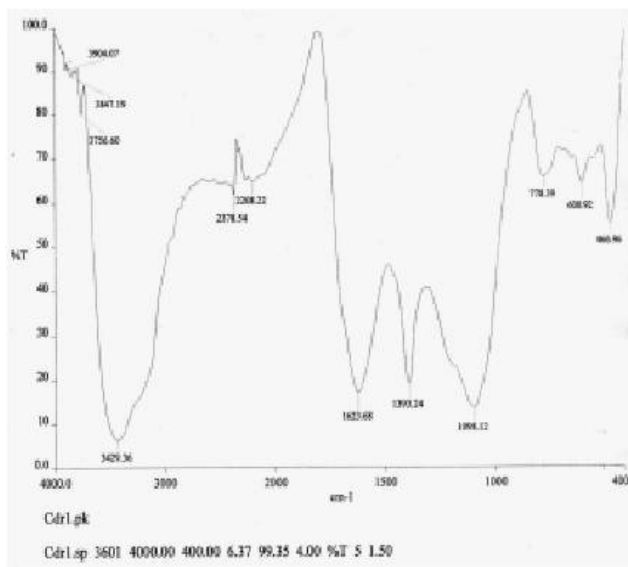
Figure 8. Effect of initial pH on the adsorption of malachite green by CBC
[MG]=45mg/l; Adsorbent dose =25mg/50ml; Contact time = 60minutes, Temperature = 35°C

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Figure 10a. FT-IR Spectra for the raw *Cynodon dactylon* activated carbon
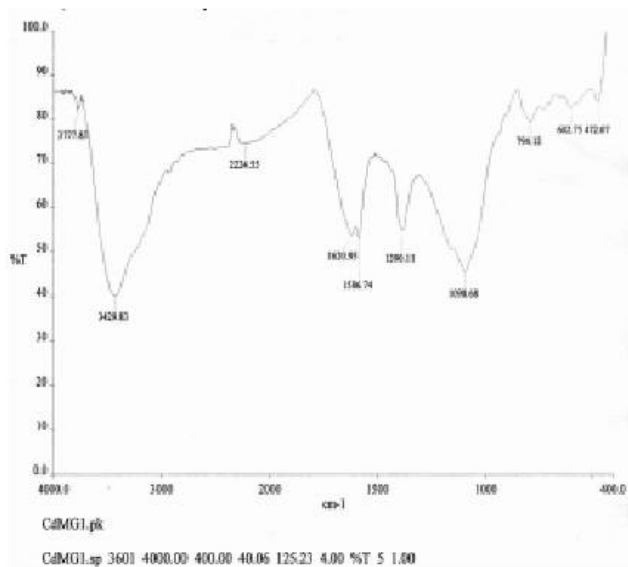

Figure 10b. FT- IR Spectra for the adsorption of malachite green by CBC
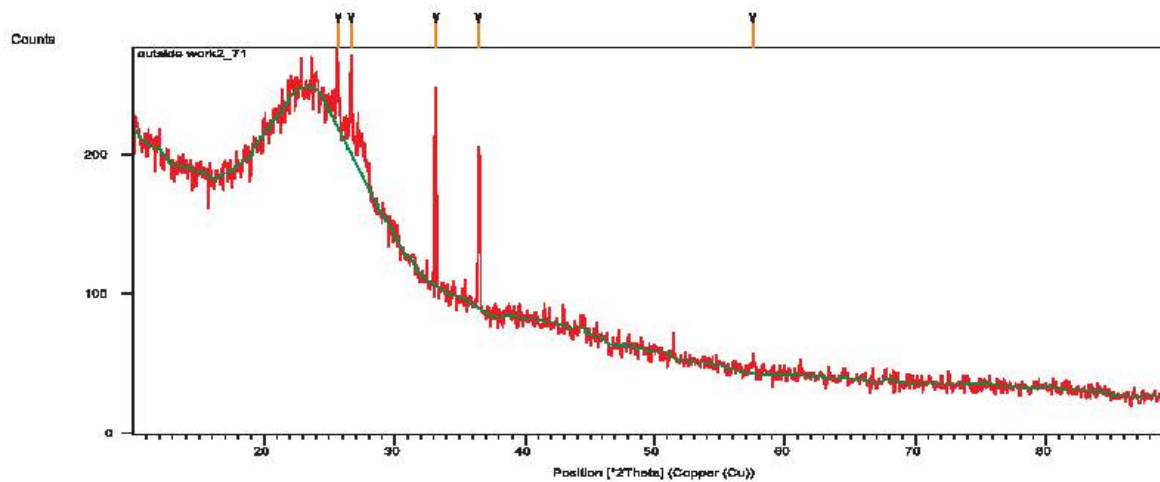

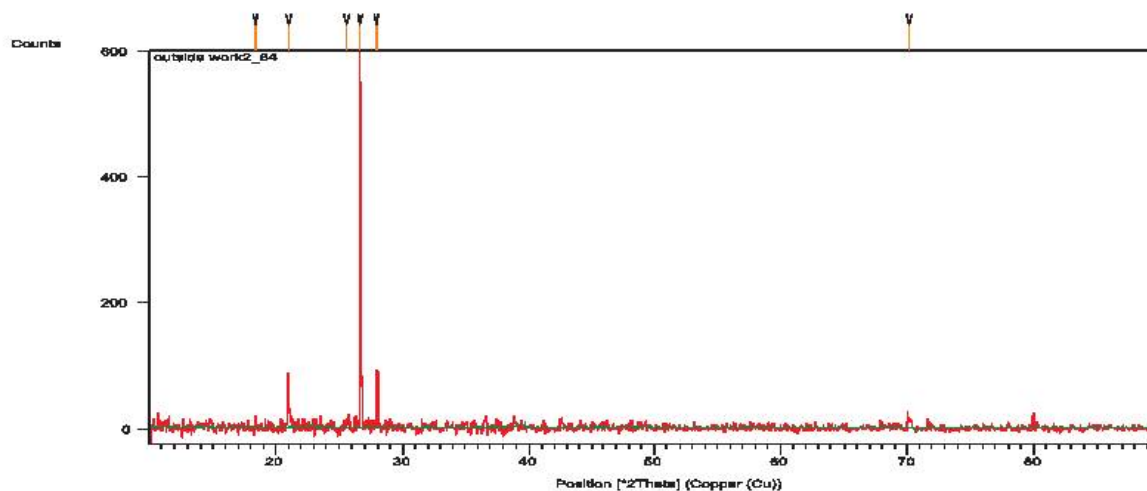**Figure 11a.** FT-IR Spectra for the raw *Cynodon dactylon* activated carbon

Figure 11b. FT-IR Spectra for the adsorption of malachite green by CBC

Effect of the ionic strength on the adsorption of malachite green on CBC

The effect of sodium chloride on the adsorption of malachite green on CBC is shown in Fig. 9. In a low solution concentration NaCl had little influence on the adsorption capacity. At higher ionic strength the
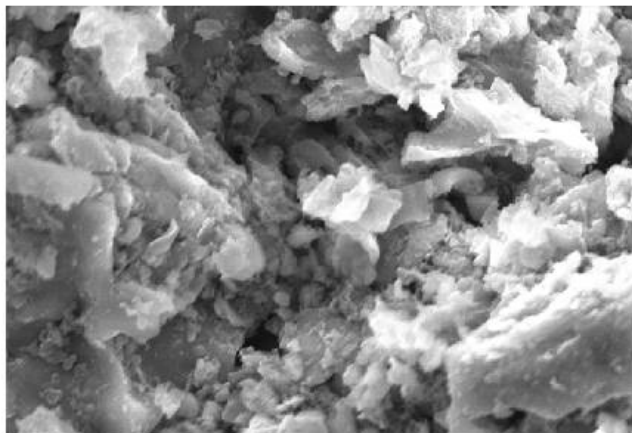

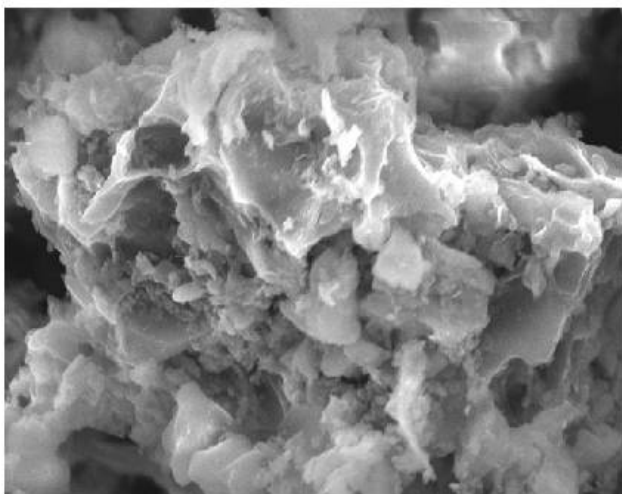**Figure 12a.** SEM Images for the Raw *Cynodon dactylon* activated carbon

Figure12b. SEM images for the adsorption of malachite green by CBC

adsorption of Malachite green increased due to the partial neutralization of the positive charge on the carbon surface and a consequent compression of the electrical double layer by the Cl⁻ anion. The chloride ion can also enhance adsorption of malachite green ion by CBC by pairing of their charges and hence reducing the repulsion between the malachite green molecules adsorbed on the surface. This could initiate carbon to adsorb more of positive malachite green ions (Yupeng Guo *et al.*, 2005; Tahir and Naseem rauf, 2006 and Arivoli, 2007).

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. If the adsorbed dyes can be desorbed using neutral pH water, then the attachment of the dye of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorp the dye then the adsorption is by ion exchange. If organic acids, like acetic acid can desorp the dye, then the dye has been held by the adsorbent through chemisorption. The effect of various reagents used for desorption studies indicated that hydrochloric acid is a better reagent for desorption, because we could get more than 78% removal of adsorbed dye. The reversibility of adsorbed dye in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of malachite green dye by mineral acids and alkaline medium indicated that the dyes were adsorbed by the activated carbon through physisorption mechanisms (Yupeng Guo *et al.*, 2005; Tahir and Naseem rauf, 2006 and Arivoli *et al.*, 2007).

Evidences for adsorption

The IR spectra of the raw activated carbon and after adsorption of malachite green have shown in Figures 10a and 10b. It could be seen that there is a slight reduction of stretching vibration adsorption bands. This clearly indicated the adsorption of dye on the adsorbent by physical forces (Arivoli, 2007 and Sudha *et al.*, 2007).

The XRD diagrams of activated carbon and malachite green adsorbed carbon are shown in Figures 11a and 11b. The intense main peak showed the presence of highly organized crystalline structure of raw activated carbon (Arivoli, 2007 and Sudha *et al.*, 2007). After the adsorption of dye, the intensity of the highly organized peak is slightly diminished. This could be attributed to the adsorption of malachite green on the upper layer of the crystalline structure of the carbon surface by means of physisorption.

The SEM diagrams of raw activated carbon and dye-adsorbed activated carbon are shown in Figures 12a and 12b. The bright spots showed the presence of tiny holes on the crystalline structure of raw activated carbon, after treatment with dye, the bright spots became black, which showed the adsorption of the malachite green on the surface of the carbon by means of physisorption (Arivoli, 2007 and Sudha *et al.*, 2007).

CONCLUSIONS

Cynodon dactylon Carbon has been available in different parts of India. In the present study, CBC was selected as a local, cheaper and readily available adsorbent for the removal of malachite green oxalate in the aqueous solutions. Adsorption of the dye was studied by batch technique and it was observed that >90% of dye removal was achieved by using 0.025 g of CBC. The kinetics of

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adsorption developed can be used to achieve low levels of dye in aqueous solutions utilizing CBC. Almost 90% removal of dye was observed at pH of 9. The adsorption data seemed to follow the Langmuir and Freundlich isotherm.

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