

# Adsorption Thermodynamics of Malachite Green dye against acid activated

## carbon

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## Abstract

The ability of *Samanea saman* Carbon (SSC) to remove malachite green from aqueous solutions has been studied for different adsorbate concentrations by varying the amount of adsorbent, temperature, pH and shaking time. Maximum adsorption of the dye, i.e. >90% has been achieved in aqueous solutions using 0.025g of *Samanea saman* carbon at a pH of 9. Thermodynamic parameters such as  $\Delta$ H°,  $\Delta$  S°, and  $\Delta$  G°, were calculated from the slope and intercept of the linear plots of lnK<sub>0</sub> against 1/T. Analysis of adsorption results obtained at 308, 318, 328 and 338 K showed that the adsorption pattern on *Samenea saman* Carbon (SSC) seems to follow the Langmuir and Freundlich isotherms. The numerical values of sorption free energy indicate physical adsorption. The kinetic data indicated an intraparticle diffusion process with sorption being first order. The mechanism of adsorption for that malachite green onto carbon have investigated by using the experimental results and confirmed by FT- IR, XRD and SEM images. The adsorbent was found to be both effective and economically viable.

**Key words:** Activated carbon (SSC), Adsorption isotherm, Equilibrium, Kinetic and Thermodynamic parameters, Intraparticle diffusion, Malachite green (MG), Regeneration pattern

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## INTRODUCTION

Out of many contaminants present in wastewater, such as acids, bases, toxic organic and inorganic dissolved solids, and colors, Colors are considered the most undesirable and are mainly caused by dyes (Gupta et al., 2005). Dyes are synthetic aromatic watersoluble dispersible organic colorants, having potential application in various industries. The dyestuff usage has been increased day by day because of tremendous increase of industrialization and man's urge for color (Mohan et al., 2002). Removal of color from dye bearing wastewater is a complex problem because of difficulty in treating such wastewaters by conventional treatment methods (Kumar et al., 2006). Synthetic dyestuffs are used extensively in textile, paper, printing industries and dye houses. The effluents of these industries are highly colored and the disposal of these wastes into receiving waters causes damage to the environment. Dyes may significantly affect

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photosynthetic activity in aquatic life because of reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics and metals, chlorides, etc. Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade (Aksu, 2005). In some cases, traditional biological procedures were combined with chemical or physical treatment processes to achieve better decolorization. Ozonation, photooxidation, electrocoagulation, adsorption, activated carbon, froth flotation, reverse osmosis, ion exchange, membrane filtration and flocculation, are applied for color removal from textile effluents (Gupta et al., 2004; Jain et al., 2003; Mittal et al., 2008). These chemical or physical chemical methods are less efficient, costly, of limited applicability and produce wastes, which are difficult to dispose of. As a viable alternative, biological processes have received increasing interest owing to their cost, effectiveness, ability to produce loss sludge and environmental benignity (Chen et al., 2003). Biological processes have potential to convert or degrade the pollutant into water, carbon dioxide and various salts of inorganic nature. The isolation of

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potent species and there by degradation is one of the interest in biological aspect of effluents treatment (Mohan *et al.*, 2002).

In recent years a number of studies have focused on some microorganisms that are able to biodegrade and biosorb dyes in wastewaters. A wide variety of microorganisms are capable of decolorization a wide range of dyes include some bacteria: Escherichia coli NO<sub>3</sub> (Chang and Kuo, 2000), Pseudomonas luteola (Chang et al., 2001), Aeromonas hydrophila (Chen et al., 2003), Kurthia species (Sani and Banerjee, 1999); fungi: Aspergillus niger (Fu and Viraraghavan, 2002), Phanerochaete chrysosporium Aspergillus terricola (Saikia and Gopal, 2004), P. chrysosporium (Four- nier et al., 2004); algae: Spirogyra species (Gupta et al., 2006), Chlorella vulgaris(Acuner and Dilek, 2004), Lemna minuscula (Valderama et al., 2002), Scenedesmus obliguus, C. pyrenoidosa and Closterium lunula (Yan and Pan, 2004).

Malachite Green (MG) is a triphenyl methane dye, which is most widely used for coloring purpose, amongst all other dyes of its category (Gupta *et al.*, 2004). MG has properties that make it difficult to remove from aqueous solutions. If the solution containing MG discharged into receiving streams it will affect the aquatic life and cause detrimental effects in liver, gill, kidney, intestine and gonads. In humans, it may cause irritation to the gastrointestinal tract upon ingestion. Contact of MG with skin causes irritation and redness and pain. Upon contact with eye will lead to permanent injury of human eyes and laboratory animals (Kumar *et al.*, 2005).

The present study undertaken to evaluate the efficiency of a carbon adsorbent prepared from acid activated *Samenea saman* Carbon (SSC) 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 masstransfer models for the adsorption of Malachite green onto acid activated carbon.

## MATERIALS

#### Adsorbent Materials

The dried *Samanea saman* 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.

## Adsorption dynamic experiments

#### Batch equilibration method

The adsorption experiments were carried out in a batch process at 35, 45, 55 and  $65\acute{\mathrm{U}}$  C temperatures. The known weight of adsorbent material was added to 50 ml of the dye solutions with an initial concentration of 10 mg/L to 60 mg/L. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 125 rpm. The solution was then filtered at preset time intervals and the residual dye concentration was measured.

#### Effect of variable parameters

#### Dosage of adsorbent

The various doses of the adsorbents are mixed with the dye solutions and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

#### Initial concentration of dye

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 10 to 60 mg/L. All other factors are kept constant.

#### **Contact time**

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.

## pН

Adsorption experiments were carried out at pH 3, 4, 5, 6, 7, 8 and 9. The acidic and alkaline pH of the media was maintained by adding the required amounts of dilute hydrochloric acid and sodium hydroxide solutions. The parameters like particle size of the adsorbents, dye concentration, dosage of the adsorbent and concentration of other ions have kept constant while carrying out the experiments. The pH of the samples was determined using a portable pH meter, Systronics make. The pH meter was calibrated with 4.0 and 9.2 buffers.

## Chloride

The experiments were done in the presence of varying chloride environments using various sodium chloride solutions. While doing the experiments, the absence of other anions has ensured.

## Temperature

The adsorption experiments were performed at four different temperatures viz., 35, 45, 55 and  $65^{\circ}$ C in a

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thermostat attached with a shaker, Remi make. The constancy of the temperature was maintained with an accuracy of  $\pm 0.5^{\circ}$  C.

#### Zero point charge

The pH at the potential of zero charge of the carbon (pHzpc) was measured using the pH drift method (Jia and Thomas, 2002). The pH of the solution was adjusted by using 0.01 M sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 25°C to remove the dissolved carbon dioxide. 50 mg of the activated carbon was added to 50 ml of the solution. After stabilization, the final pH was recorded. The graphs of final pH versus initial pH used to determine the zero point charge of the activated carbon.

#### **Titration studies**

According to Boehm (Jia and Thomas, 2002) only strong acidic carboxylic acid groups are neutralized by sodium bicarbonate, where as those neutralized by sodium carbonate are thought to be lactones, lactol and carboxyl group. The weakly acidic phenolic groups only react with strong alkali, sodium hydroxide. Therefore, by selective neutralization using bases of different strength, the surface acidic functional group in carbon can be characterized both quantitatively and qualitatively. Neutralization with hydrochloric acid characterizes the amount of surface basic groups that are, for example, pyrones and chromenes. The basic properties have described to surface basic groups and the pi electron system of carbon basal planes. The results indicate that the activated carbon used may possess acidic oxygen functional group on their surface and this is supported well by their respective zeropoint charge values. The results obtained from the above characterization studies are given in the Table 1.

#### **Desorption studies**

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. The effect of various reagents used for desorption are studied.

#### **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 discussions**

#### Characterization of the adsorbent:

Activated carbons are a widely used adsorbent due to its high adsorption capacity, high surface area, micro porous structure and high degree of surface respectively. The wide usefulness of carbon is a result

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of their specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determines the sorption activity. The physico-chemical properties of the chosen adsorbent are listed in following Table 1.

Table 1. Characteristics of the adsorbent

Properties	SSC
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
pHzpc	5.4
Surface groups (m equiv/g)	94
i) Carboxylic acid	0.325
ii) Lactone, lactol	0.074
iii) Phenolic	0.067
iv) Basic (pyrones and chromenes)	0.026

#### Effect of carbon concentration

The adsorption of the MG dye on carbon was studied by varying the carbon concentration (10-100 mg/50ml) for 40 mg/L of dye concentration. The percent adsorption increased with increase in the carbon concentration (Figure 1). This was attributed to increase carbon surface area and availability of more adsorption sites (Namasivayam *et al.*, 1996; Namasivayam and Yamuna, 1995). Hence, the entire studies are carried out with the adsorbent dose of 50 mg of adsorbent /50 ml of the adsorbate solution.



**Fig.1.** Effect of adsorbent dose on the adsorption of MG by SSC [MG] = 30 mg/L; pH = 6.5; Contact time = 60 min

## Effect of contact time and initial MG concentration

The experimental results of adsorptions of at various concentrations with contact time are shown in the figure (Figure 2). The equilibrium data were presented in the table (Table 2) revealed that, percent of adsorption decreased with increase in initial MG concentration, but the actual amount of MG adsorbed per unit mass of carbon increased with increase in MG concentration. It means that the adsorption was highly dependent on initial concentration of MG. It was because of that at lower concentration, the ratio of the initial number of MG molecules to the available surface area was low. Subsequently, the fractional adsorption becomes independent of initial concentration. However, at high concentration, the available sites of adsorption become fewer and hence the percentage removal of MG was dependent upon initial concentration (Namasivayam et al., 1996;

Namasivayam and Yamuna, 1995). Equilibrium have established at 60 minutes for all concentrations (Figure 2) revealed that, the curves are single, smooth and continuous; it was leading to saturation, suggesting the possible monolayer coverage of the MG on the carbon surface.

#### Adsorption isotherm

The Langmuir adsorption isotherm (Langmuir, 1918) of the MG at 35, 45, 55 and 65æ%C using the SSC was showed in the figure (Fig 3). The Langmuir equation assumes that there was no interaction between the adsorbate molecules and that the sorption was localized in a monolayer. It was then assumed that once a dye molecule occupies a site, no further sorption can take place at that site. Theoretically, therefore, a saturation value was reached; beyond which no further sorption can take place. Compared to the

Table - 2. Equilibrium parameters for the adsorption of MG by SSC

MG	Temp., °C												
concentration mg/L	35	45	55	65	35	45	55	65	35	45	55	65	
-	(	C <sub>e</sub> (1	ng/L)		Q <sub>e</sub> (mg/g)					MG Removed (%)			
10	1.9728	1.7457	1. <mark>5</mark> 329	1.3128	4.0136	4.1271	4.2335	4.3436	80.2	82.5	84.6	86.8	
20	4.5842	4.3029	4.0984	3.8728	7,7079	7.8485	7.95 <mark>0</mark> 8	8.0636	77.0	78.4	79.5	80.6	
30	8.7246	8.5182	8.3027	8.1011	10.6377	10.7409	10.8486	10.9494	70.9	71.6	72.3	72.9	
40	14.4928	14.2757	14.0252	13.8722	12.7536	12.8621	12.9874	13.0939	63.7	64.3	64.9	65.4	
50	21.8526	21.6331	21.4139	21.2094	14.0735	14.1831	14.2930	14.3953	56.2	56.7	57.1	57.5	
60	27.5972	27.3849	27.1798	26.8729	16.2014	16.3075	16.4105	16.5635	54.0	54.3	54.7	55.2	





**Fig.2.** Effect of contact time on the adsorption of MG by SSC [MG] = 30 mg/L; Dose = 50 mg/50 ml; pH = 6.5

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MG by SSC

Langmuir isotherm, the Freundlich (Freundlich, 1906) model was generally found to be better suited for characterizing multi-layer adsorption process. The Langmuir parameters,  $(Q_m)$  and (b) were computed from the slopes and intercepts of the straight lines of plot of  $(C_e/Q_e)$  vs  $C_e$  (Fig.3), while the values of Freundlich constants, i.e.  $K_{f}$  and 1/n were calculated from the plots (Fig. 4) of  $\log C_a$  against  $\log Q_a$ . (Q<sub>m</sub>) and (b) are Langmuir constants related to absorption capacity and energy of adsorption, respectively, while  $K_{f}$  indicated the adsorption capacity and 1/n was indicative of the intensity of reaction (Freundlich, 1906). Parameters of the Langmuir and Freundlich isotherms are computed in the tables (Table 3 and 5) the essential characteristics of a Langmuir constant separation factor or equilibrium parameter,  $R_{I}$ . The value of  $R_{I}$ , calculated from the above expression shown in the table (Table 4) lies in the range of 0.434 to 0.081, indicated favourable adsorption of MG oxalate on SSC for all studied concentrations.

## Table - 3. Langmuir isotherm results for the adsorption of MG by SSC

S.No. Temp. °	T 90	Statistical	Langmuir constan				
	Temp. C	parameter, r <sup>2</sup>	Qm	b			
1.	35	0.9958	20.09	0.1275			
2.	45	0.9956	19.59	0.1455			
3.	55	0.9953	19.22	0.1647			
4.	65	0.9941	18.92	0.1866			

**Table 4.** Dimensionless separation factor  $(R_L)$  for the<br/>adsorption of MG by SSC

MG	Temp., °C								
(mg/L)	35	45	55	65					
10	0.434	0.400	0.377	0.3 <mark>4</mark> 4					
20	0.277	0.250	0.232	0.208					
30	0.204	0.181	0.168	0.149					
40	0.161	0.142	0.132	0.116					
50	0.133	0.117	0.108	0.095					
60	0.113	0.100	0.091	0.081					

**Table 5.** Freundlich isotherm results for the<br/>adsorption of MG by SSC

S.No.	Temp., °C	Statistical	Freundlich constants			
	parameter, r <sup>2</sup>	K <sub>f</sub>	n			
1.	35	0.9819	1.6525	1.9905		
2.	45	0.9843	1.6080	2.1048		
3.	55	0.9873	1.5706	2.2148		
4.	65	0.9904	1.5314	2.3463		

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## Kinetics of adsorption

The adsorption of MG dye from an aqueous follows reversible first order kinetics, when a single species are considered on a heterogeneous surface. The rate constants  $(K_{d})$  for the adsorption processes have been calculated from the slope of the linear plots of  $\log C_0/$ C, versus t for different concentrations and temperatures. The rate constant values were presented in the table (Table 7) showed that the rate constant  $(k_{a})$  increases with increase in temperature suggesting that the adsorption process in endothermic in nature. Further, k<sub>ad</sub> values decrease with increase in initial concentration of the dye. 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 relationship between initial dye concentration and rate of reaction will not be linear. Thus, in the present study pore diffusion limits the overall rate of dye adsorption. The overall rate of adsorption was separated into the rate of forward and reverse reactions using the above equation. The rate constants for the forward and reverse processes are also presented in the table (Table 7) indicated that, at all initial concentrations and temperatures, the forward rate constant was much higher than the reverse rate constant suggesting that the rate of adsorption was clearly dominant (Arivoli, 2007; Arivoli and Hema, 2007; Arivoli et al., 2007).

## **Effect of temperature**

The adsorption capacity of the carbon increased with increase in the temperature of the system from 35° to 65°C. The  $\Delta$  H° and  $\Delta$  S° values obtained from the slope and intercept of van't Hoffs plots have presented in the table (Table 6). The values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$ and  $\Delta G^{\circ}$  were calculated as previously. Positive values of  $\triangle$  H° and  $\triangle$  S° suggested endothermic reaction, while the negative values of free energy change ( $\Delta G^{\circ}$ ) indicated that the adsorption was spontaneous (Table 6). The positive values of  $\Delta S^{\circ}$  suggested the increased randomness at the solid-solution interface during desorption of MG oxalate on SSC. In desorption of the dye, the adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than was lost by the adsorbate ions, thus allowing for the prevalence of randomness in the system (Arivoli and Hema, 2007; Arivoli et al., 2007; Renmin Gong, 2005).

## Effect of pH

The influence of pH on the dye adsorption by SSC was studied while the MG concentration, shaking time and amount of adsorbent were fixed. The variation of MG adsorption on SSC over a pH range of 3-9 was shown in the figure (Fig.6). The result revealed that the adsorption of the MG increases 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 MG the adsorbent surface was primarily influenced by the surface charge on the adsorbent, which was in turn influenced by the solution pH. The  $pH_{zpc}$  value for SSC was 6.5. At pH values below, pH<sub>zpc</sub> the adsorbent had net positive charge and would, therefore, be prone to electro statically repel cations. MG was 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 was attracted by an anionic adsorbent.

	Table 6. Equilibrium constant and thermoo	lynamic	parameters for the adsorp	otion of MG b	y activated SSC
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MG				Tem	<mark>9., °</mark> C				$\Delta \mathbf{H}^{\circ}$	ΔS°
(mg/L)	35	45	55	65	35	45	55	65	KJ/mol	KJ/mol
		K	lo l			-∆G°	1			
10	4.06	4.72	5.52	6.61	3.53	4.03	4.58	5.22	13.16	54.98
20	3.36	3.64	3.87	4.16	3.05	3.36	3.63	3.94	5.94	29.68
30	2.43	2.52	2.61	2.70	2.23	2.40	2.57	2.74	2.93	17.04
40	1.75	1.80	1.85	1.88	1.42	1.53	1.65	1.74	1.88	10.91
50	1.28	1.31	1.33	1.35	0.63	0.70	0.76	0.83	1.31	6.41
60	1.17	1.20	1.22	1.23	0.39	0.49	0.53	0.57	1.26	5.50

Table 7. Rate constants for the adsorption of MG (10<sup>3</sup> k<sub>ad</sub>, min<sup>-1</sup>) and the constant for forward (10<sup>3</sup> k<sub>1</sub>, min<sup>-1</sup>) and reverse (10<sup>3</sup> k<sub>2</sub>, min<sup>-1</sup>) process

MG	Temp., °C											
(mg/L)	35	45	55	65	3	5	45	5		55	65	5
		K	ad		k <sub>1</sub>	<b>k</b> <sub>2</sub>	$\mathbf{k}_1$	<b>k</b> <sub>2</sub>	<b>k</b> <sub>1</sub>	$\mathbf{k}_2$	k <sub>1</sub>	k <sub>2</sub>
10	9.06	10.23	11.49	12.72	7.28	1.78	8.45	1.77	9.73	1.76	11.06	1.66
20	4.09	4.37	4.53	4.52	3.15	0.94	3.43	0.93	3.65	0.88	3.66	0.86
30	2.27	2.45	2.36	2.37	1.61	0.66	1.76	0.69	1.71	0.65	1.74	0.63
40	1.38	1.36	1.41	1.41	0.88	0.50	0.87	0.49	0.92	0.48	0.93	0.48
50	0.95	0.97	0.98	0.92	0.54	0.41	0.55	0.42	0.52	0.42	0.59	0.33
60	0.71	1.18	0.73	0.75	0.38	0.33	0.64	0.54	0.41	0.33	0.42	0.33



Fig.5. Intraparticle diffusion effect for the adsorption of MG by SSC [MG] = 30 mg/L; Contact time = 60 min; pH = 6.5



Fig.4. Linear Freundlich isotherm for the adsorption of MG by SSC

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**Fig.6.** Effect of Initial pH on the adsorption of MG by SSC [MG] = 30 mg/L; Dose = 50mg/50 ml; Contact time = 60 min



**Fig.7.** Effect of Chloride ions on the adsorption of MG by SSC [MG] = 30 mg/L; Adsorbent dose = 50 mg/50ml; Temp = 35°C



Fig.8a. FT-IR Spectra for Raw SSC

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Fig.8b. FT-IR Spectra for the adsorption of MG by SSC



Fig.9a. XRD Spectra for Raw SSC



Fig.9b. XRD Spectra for the adsorption of MG by SSC

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Fig.10a. SEM images for Raw SSC

#### Intraparticle diffusion

The most commonly used technique for identifying the mechanism involved in the sorption process was by fitting the experimental data in an intraparticle diffusion plot. Previous studies by various researchers showed that the plot of Q, versus t<sup>0.5</sup> represents multi linearity, which characterizes the two or more steps involved in the sorption process. An intraparticle diffusion coefficient  $K_p (mg/g min^{0.5})$  value can be obtained from the slope of the plot of  $Q_t(mg/g)$  versus t<sup>0.5</sup> for MG. From the figure (Figure 5), 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 (Vadivelan and Vasantha Kumar, 2005, Weber, 1967). The initial curved portion of the plot indicated a boundary layer effect while the second linear portion was due to intraparticle or pore diffusion. The slope of the second linear portion of the plot has been defined as the intraparticle diffusion parameter,  $K_p(mg/gmin^{0.5})$ . 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<sub>p</sub> value was given by 0.042, 0.072, 0.099, 0.125 and 0.167 mg/g min<sup>0.5</sup> for initial dye concentration of 10 to 60 mg/L at 35°C.

In carbon-aqueous systems the potential of the surface was 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<sup>-</sup> and complex ions formed by bonding with  $H^+$  and OH<sup>-</sup>. The broken bonds along the surface of the carbon result in hydrolysis.

At low pH the reaction might be:

SSC-OH + H<sup>+</sup>  $\rightarrow$  SSC-OH<sup>+2</sup>

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Fig.10b. SEM images for the adsorption of MG by SSC

At high pH the reaction was:

SSC-OH + OH  $\rightarrow$  SSC-O  $\cdot$  + H<sub>2</sub>O

In the present investigation, the adsorption was maxima at pH9. Therefore, at high pH, the solution in contact with the basal oxygen surface of the tetrahedral sheet will contain excess hydroxyls. The surface will then exhibit a cation exchange capacity (Tahir and Naseem Rauf, 2006; Yupeng Guo, *et al.*, 2005; Sreedhar and Anirudhan, 1999).

## Effect of the ionic strength on the adsorption of MG on SSC

The effect of sodium chloride on the adsorption of MG on SSC was shown in the figure (Fig.7). In a low solution concentration, NaCl had little influence on the adsorption capacity. At higher ionic strength, the adsorption of MG will be increased due to the partial neutralization of the positive charge on the carbon surface and a consequent compression of the EDL by the Cl<sup>-</sup> anion. The chloride ion can also enhances adsorption of MG ion by SSC by pairing of their charges and hence reducing the repulsion between the MG molecules adsorbed on the surface. This initiates carbon to adsorb more of positive MG ions (Arivoli, 2007; Tahir and Naseem Rauf, 2006; Yupeng Guo, *et al.*, 2005).

#### **Desorption studies**

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. The effect of various reagents used for desorption studies indicated that hydrochloric acid was a better reagent for desorption, because it could get more than 78% removal of adsorbed dye. The reversibility of adsorbed dye in mineral acid or base was in agreement with the pH dependent results obtained. The desorption of MG dye by mineral acids and alkaline medium indicated that the dyes were adsorbed by the activated carbon through by physisorption mechanisms (Arivoli *et al.*, 2007, Yupeng Guo, *et al.*, 2005; Sreedhar and Anirudhan, 1999).

#### **Evidences for adsorption**

The IR spectra of the raw activated carbon and after adsorption of MG have shown in the figures (Figure 8a and 8b). It could be seen that the slight reduction of stretching vibration adsorption bands. This clearly revealed that the adsorption of dye on the adsorbent by physical forces (Arivoli, 2007; Arivoli *et al.*, 2007).

The XRD diagrams of activated carbon and MG adsorbed carbon have shown in the figures (Figure 9a and 9b). The intense main peak showed the presence of highly organized crystalline structure of raw activated carbon (Arivoli, 2007; Arivoli *et al.*, 2007), after the adsorption of dye, the intensity of the highly organized peaks are slightly diminished. This has attributed to the adsorption of MG 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 have shown in the figures (Figure 10a and 10b). 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 indicated that the adsorption of the MG on the surface of the carbon by means of physisorption (Arivoli, 2007; Arivoli *et al.*, 2007).

## CONCLUSIONS

Samanea saman Carbon has been available in different parts of the country. In the present study, SSC was selected as a local, cheaper and readily available adsorbent for the removal of Malachite green oxalate from 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 0.025g of SSC. The kinetics of adsorption developed can be used to achieve low levels of dye from aqueous solutions utilizing SSC. Almost 90% removal of dye was observed at pH of 9. The adsorption data seems to follow the Langmuir and Freundlich isotherms.

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