Available on line www.jocpr.com

Journal of Chemical and Pharmaceutical Research

ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2011, 3(2):637-649

Adsorption Thermodynamics of Malachite Green Dye onto Acid Activated Low Cost Carbon

B. R. Venkatraman[1*], K. Hema[2], V. Nandhakumar[3] and S. Arivoli[4]

[1]*PG & Research Department of Chemistry, Periyar E. V. R. College (Autonomous), Tiruchirapalli*
[2]*Department of Chemistry, Saveetha School of Engineering, Saveetha University, Thandalam, Chennai*
[3]*Department of Chemistry, A.V.V.M. Sri Pushpam College, Poondi*
[4]*Department of Chemistry, H. H. The Rajah's Government College, Pudukkottai*

ABSTRACT

The ability of Terminalia Catappa Linn carbon 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. Thermodynamic parameters such as ΔH°, ΔS°, and ΔG°, were calculated from the slope and intercept of the linear plots of $\ln K_0$ *against 1/T. Analysis of adsorption results obtained at 303, 313, 323 and 333 K showed that the adsorption pattern on Terminalia Catappa Linn carbon seems to follow the Langmuir and Freundlich. The temperature increase reduces adsorption capacity by Terminalia Catappa Linn carbon, due to the enhancement of the desorption step in the mechanism. The numerical values of sorption free energy indicate physical adsorption. The kinetic data indicated an intraparticle diffusion process with sorption being first order. The concentration of malachite green oxalate was measured before and after adsorption by using UV-Visible spectrophotometer.*

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

INTRODUCTION

The concentration and effective utilization of activated carbon generated from natural plant material have attracted worldwide attention in a view of the large disposal problem without detriment to environment. Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, saw dust, buffing dust of leather industry, coir pith, crude oil, residue tropical grass, olive stone and almond shells, pine bark, wool waste, coconut shell etc., as carbonaceous precursors for the removal of dyes from water and wastewater [1,2,3]. The present study undertaken to evaluate the efficiency of a carbon adsorbent prepared from acid activated *Terminalia Catappa Linn* carbon (TCC) 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, the applicability of kinetic and mass-transfer models for the adsorption of Malachite green onto acid activated carbon are reported in elaborately.

EXPERIMENTAL SECTION

Adsorbent Material

The dried *Terminalia Catappa Linn* fruit shells were carbonized with concentrated sulphuric acid in the weight by volume ratio of 1:1 (w/v). Heating for twelve hours in a furnace at 400°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 120°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 30, 40, 50 and 60˚ C temperatures. The known weight of adsorbent material was added to 50 ml of the dye solutions with an initial concentration of 20 mg/L to 100 mg/L. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 120 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 20 to 100 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.

pH

Adsorption experiments were carried out at pH 2, 3, 4, 5, 6, 7, 8, 9 and 10. 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., 30, 40, 50 and 60˚C in a thermostat attached with a shaker, Remi make. The constancy of the temperature was maintained with an accuracy of ± 0.5° C.

Zero point charge

The pH at the potential of zero charge of the carbon (pHzpc) was measured using the pH drift method [4]. The pH of the solution was adjusted by using 0.01 M sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 25^0C 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 [4] 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 zero point 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.

RESULTS AND DISCUSSION

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 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 are listed in Table 1.

Table 1 Characteristics of the adsorbent

Properties	**TCC**
Particle size (mm)	0.045
Density (g/cc)	0.3258
Moisture content (%)	1.85
Loss on ignition (%)	82
Acid insoluble matter (%)	3
Water soluble matter (%)	0.78
pH of aqueous solution	7.00
pH_{zpc}	6.15
Surface groups (m equiv/g)	
i) Carboxylic acid	0.323
ii) Lactone, lactol	0.065
iii) Phenolic	0.058
iv) Basic (pyrones and chromenes)	0.032

Effect of contact time and initial dye concentration

The experimental results of adsorptions of at various concentrations (20, 40, 60, 80 and 100 mg/L) with contact time are shown in representative Figure 1. The equilibrium data were collected in Table 2 reveals that, percent adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of carbon increased with increase in dye concentration. It means that the adsorption is highly dependent on initial concentration of dye. It is because of that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentration [5,6]. Equilibrium have established at 40 minutes for all concentrations. Figure 1 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dyes on the carbon surface.

Table 2- Equilibrium parameters for the adsorption of Dye onto activated Carbon

$[MG]_0$		**C_e (mg/L)**				**Q_e (mg/g)**					**Dye removed (%)**				
Temperature (C)															
		30^o	**40^o**	**50^o**	**60^o**		**30^o**	**40^o**	**50^o**	**60^o**		**30^o**	**40^o**	**50^o**	**60^o**
20		2.5725	2.2532	2.0132	1.5835		17.4275	17.7468	17.9868	18.4165		87.1	88.7	89.9	92.1
40		6.8234	6.3324	5.8254	5.3136		33.1766	33.6676	34.1746	34.6864		82.9	84.1	85.4	86.7
60		14.9832	13.9735	12.9835	11.9772		45.0168	46.0265	47.0165	48.0228		75.0	76.7	78.3	80.0
80		28.4353	26.9832	25.4835	24.0012		51.5647	53.0168	54.5165	55.9788		64.4	66.2	68.1	69.9
100		42.5432	39.5235	36.5433	33.5221		57.4568	60.4765	63.4565	66.4779		57.4	60.4	63.4	66.5

Table 3 - Langmuir isotherm results

Dye		**Temp**		**Statistical parameters/constants**				
		^{0}C		**r^2**		**Q_m**		**b**
MG		30		0.9882		65.17		0.1401
		40		0.9865		66.99		0.1438
		50		0.9895		72.97		0.1605
		60		0.9875		74.96		0.1663

Table 4 Dimensionless Separation factor (R_L)

				Temperature (^{0}C)				
$[MG]_0$ (mg/L)		**30**		**40**		**50**		**60**
20		0.263		0.257		0.238		0.231
40		0.151		0.148		0.134		0.131
60		0.106		0.104		0.094		0.091
80		0.081		0.079		0.072		0.070
100		0.066		0.064		0.058		0.058

Table 5 - Freundlich isotherm results

Dye		**Temp**		**Statistical parameters/constants**				
		^{0}C		**r^2**		**K_f**		**n**
MG		30		0.9850		1.5096		2.4308
		40		0.9895		1.5219		2.3203
		50		0.9865		1.5318		2.3472
		60		0.9925		1.5442		2.7191

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

$[MG]_0$		**K_0**					**ΔG^o**					**ΔH^o**		**ΔS^o**
							Temperature (^{0}C)							
		30^o	**40^o**	**50^o**	**60^o**		**30^o**	**40^o**	**50^o**	**60^o**				
20		6.77	7.87	8.93	11.63		-4.81	-5.37	-5.88	-6.79		14.06		63.22
40		4.86	5.32	5.86	6.52		-3.98	-4.34	-4.48	-5.19		8.16		39.99
60		3.00	3.29	3.62	4.01		-2.77	-3.10	-3.45	-3.84		7.94		35.29
80		1.81	1.96	2.13	2.33		-1.49	-1.75	-2.04	-2.34		6.97		27.90
100		1.35	1.53	1.73	1.98		-0.75	-1.12	-1.48	-1.89		4.60		16.42

Table 7 - Rate constants for the adsorption of Malachite green dye (10^3 k_{ad}, min $^{-1}$) and the constants for forward (10^3 k_1, min $^{-1}$) and reverse (10^3 k_2, min^{-1}) process

							Temperature (^{0}C)										
$[D]_0$		**k_{ad}**					**30**			**40**			**50**			**60**	
		30^o	**40^o**	**50^o**	**60^o**		**k_1**	**k_2**		**k_1**	**k_2**		**k_1**	**k_2**		**k_1**	**k_2**
20		17.56	20.05	22.18	26.06		15.31	2.25		17.81	2.24		19.95	2.23		20.00	2.06
40		13.89	14.65	15.84	17.24		11.46	2.35		12.33	2.32		13.54	2.30		14.95	2.29
60		9.53	10.20	11.32	12.84		7.15	2.38		7.83	2.37		8.87	2.45		10.28	2.56
80		6.82	7.28	7.84	8.53		4.40	2.42		4.83	2.45		5.34	2.50		5.98	2.55
100		6.74	6.99	7.26	7.87		3.84	2.90		4.23	2.76		4.61	2.65		5.20	2.64

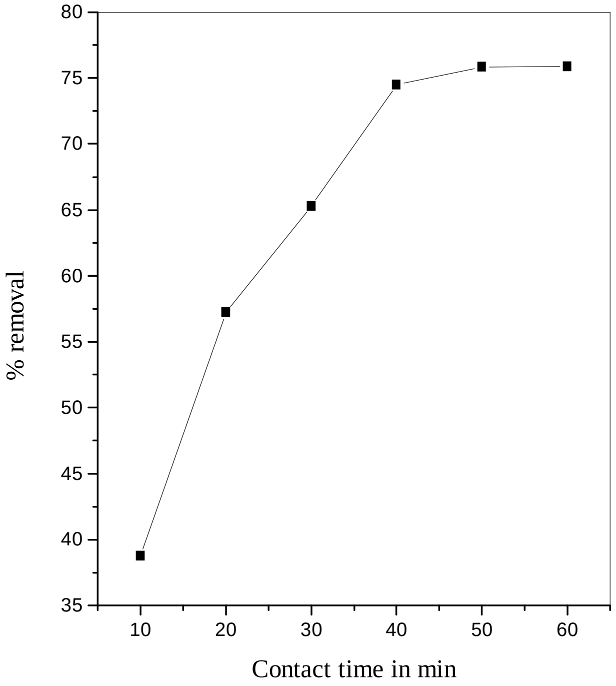

Fig.1-Effect of contact time on the adsorption of MG
[MG]=60 mg/L;Adsorbent dose= 50 mg/50 ml;pH=7

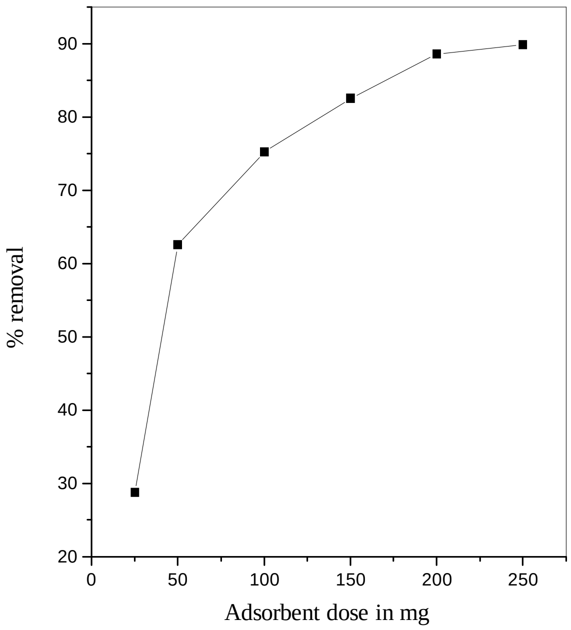

Fig.2-Effect adsorbent dose on the adsorption of MG
[MG]=60 mg/L;Contact time = 60 min;pH=7

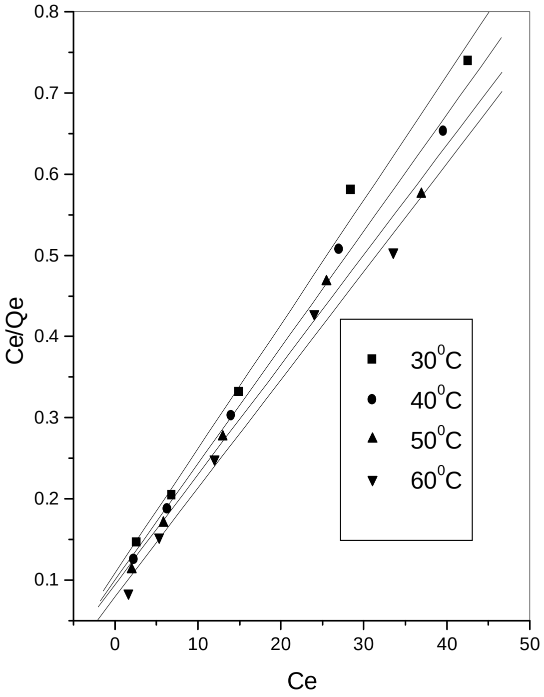

Fig.3-Langmuir adsorption isotherm for the removal of MG

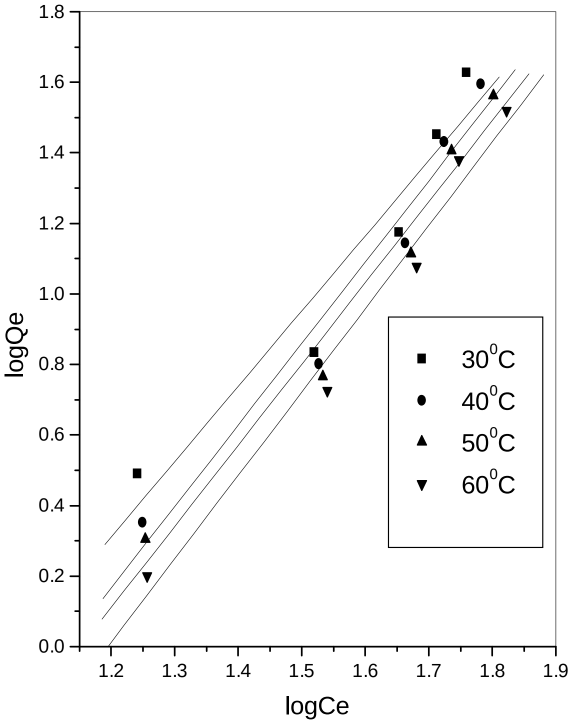

Fig.4-Freundlich adsorption isotherm for the removal of MG

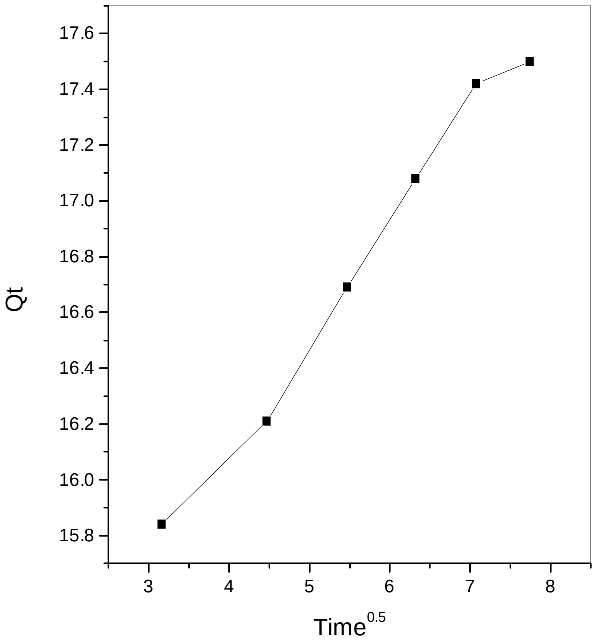

Fig.5-Intraparticle diffusion effect for the adsorption of MG
[MG]=20 mg/L;Adsorbent dose= 50 mg/50 ml;pH=7

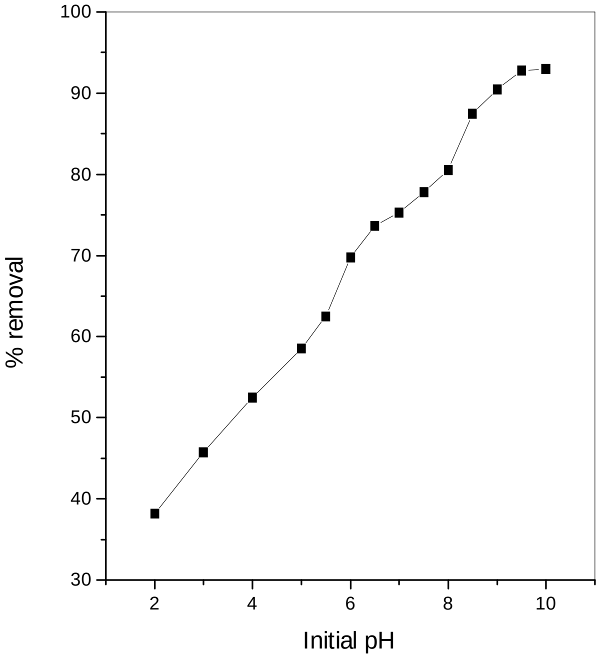

Fig.6-Effect of initial pH on the adsorption of MG
[MG]=60 mg/L;Adsorbent dose=50 mg/50 ml

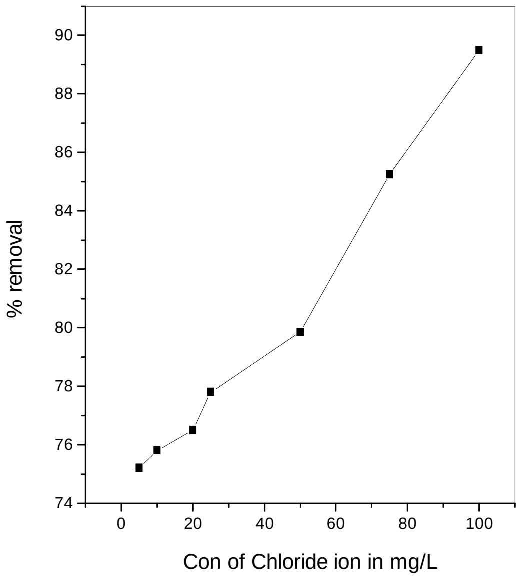

FIg.7-Effect of other ion on the adsorption of MG
[MG]=60 mg/L;adsorbent dose=50 mg/50 ml;contact time=60 min

Effect of carbon concentration

The adsorption of the Malachite green dye on carbon was studied by varying the carbon concentration (25-250 mg/50ml) for 40 mg/L of dye concentration. The percent adsorption increased with increase in the carbon concentration (Fig. 2). This was attributed to increased carbon surface area and availability of more adsorption sites [5,6]. Hence the entire studies are carried out with the adsorbent dose of 50 mg of adsorbent /50 ml of the adsorbate solution.

Adsorption isotherm

Fig 1 shows the Langmuir adsorption [7] isotherms of the dye at 303,313,323 and 333 K using the *Terminalia Catappa Linn* carbon. The Langmuir equation assumes that there is no interaction between the sorbate molecules and that the sorption is localized in a monolayer. It is then assumed that once a dye molecule occupies a site, no further sorption can take place at that site. Theoretically, therefore, a saturation value is reached; beyond which no further sorption can take place. Compared to the Langmuir isotherm, the Freundlich [8] model is 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 $\log C_e$ against $\log Q_e$. Q_m and b are Langmuir constants related to absorption capacity and energy of adsorption, respectively, while K_f indicates the adsorption capacity and l/n is indicative of the intensity of reaction [9,10,11]. Parameters of the Langmuir and Freundlich isotherms are computed in Table 3 and 4, the essential characteristics of a Langmuir constant separation factor or equilibrium parameter, R_L,

$$R_L = 1/ (1+bC_o)$$

Where b is Langmuir constant and C_e is the initial concentration of the dye [10,11]. The value of $R_{L,}$ calculated from the above expression shown in Table 5 lies in the range of 0.263-0.058, indicates favourable adsorption of malachite green oxalate on *Terminalia Catappa Linn* carbon for all studied concentrations at 303,313,323 and 333 K.)

Effect of temperature

The adsorption capacity of the carbon increased with increase in the temperature of the system from 30°-60°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:

$$K_0 = C_{solid}/C_{liquid}$$

$$\Delta G° = -RT \ln K_O$$

$$\log K_0 = \Delta S°/ (2.303RT) - \Delta H°/(2.303RT)$$

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 van't Hoff plots have presented in Table 6.

The values of $\Delta H°$ and $\Delta S°$ and $\Delta G°$ were calculated as previously. Positive values of $\Delta H°$ and $\Delta S°$ suggest endothermic reaction, while the negative values of free energy change ($\Delta G°$) indicate that the adsorption is spontaneous (Table 6) .The positive values of $\Delta S°$ suggest the increased randomness at the solid-solution interface during desorption of malachite green oxalate on *Terminalia Catappa Linn* 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 [11,12,13,14]

Kinetics of adsorption

The kinetics of sorption describes the solute uptake rate, which in turn governs residence time or sorption reaction. It is one of the important characteristics in defining the efficiency or sorption. In the present study, the kinetics of the dye removal was carried out to understand the behaviour of these low cost carbon adsorbents. The adsorption of Malachite green dye from an aqueous follows reversible first order kinetics, when a single species are considered on a heterogeneous surface.

The heterogeneous equilibrium between the dye solutions and the activated carbon are expressed as

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$$

Where k_1 is the forward rate constant and k_2 is the backward rate constant. A represents dye remaining in the aqueous solution and B represent dye adsorbed on the surface of activated carbon. The equilibrium constant (K_0) is the ration of the concentration adsorbate in adsorbent and in aqueous solution ($K_0=k_1/k_2$). In order to study the kinetics of the adsorption process under consideration the following kinetic equation proposed by Natarajan and Khalaf as cited in literature has been employed [1].

$$\log C_0/C_t=(K_{ad}/2.303)t$$

Where C_0 and C_t are the concentration of the dye in (in mg/L) at time zero and at time t, respectively. The rate constants (K_{ad}) for the adsorption processes have been calculated from the slope of the linear plots of log C_0/C_t versus t for different concentrations and temperatures. The determination of rate constants as described in literature given by

$$K_{ad}=k_1+k_2=k1+(k_1/K_0)=k_1[1+1/K_0]$$

The overall rate constant k_{ad} for the adsorption of dye at different temperatures are calculated from the slopes of the linear Natarajan-Khalaf plots. The rate constant values are collected in Table 7 shows that the rate constant (k_{ad}) increases with increase in temperature suggesting that the adsorption process in endothermic in nature. Further, k_{ad} 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 over all rate of adsorption is separated into the rate of forward and reverse reactions using the above equation. The rate constants for the forward and reverse processes are also collected in Table 7 indicate that, at all initial concentrations and temperatures, the forward rate constant is much higher than the reverse rate constant suggesting that the rate of adsorption is clearly dominant [1,11,13].

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 [16], an intraparticle diffusion coefficient K_p is defined by the equation:

$$K_p=Q/t^{0.5}$$

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 5, it was noted that the sorption process tends to be followed by two phases. The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds by surface sorption and intraparticle diffusion [15,16]. 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 the contribution of the surface sorption in the rate limiting step. The calculated intraparticle diffusion coefficient K_p value was given by 0.412, 0.448, 0.485, 0.527 and 0.564 mg/g min$^{0.5}$ for initial dye concentration of 20, 40, 60, 80 and 100 mg/L at 30^0C.

Effect of pH

The influence of pH on the dye adsorption onto *Terminalia Catappa Linn* carbon was studied while the dye concentration, shaking time and amount of adsorbent were fixed. The variation of malachite green adsorption on *Terminalia Catappa Linn* carbon over a pH range of 2.0-10.0 is shown in Figure 6. The result reveals that the adsorption of the dye increases from 38% to 95% with an increase in pH of the solution from 2.0 to 9.5 and then remains almost constant. The adsorption of these charged dye groups onto 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 *Terminalia Catappa Linn* carbon was 6.15. At pH values 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.

At low pH the reaction might be:

$$\text{Carbon-OH} + H^+ \rightarrow \text{Carbon-OH}^+_2$$

At high pH the reaction is:

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

In our studies the maximum adsorption is at pH 9.5. So 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 [17,18,19].

Effect of the ionic strength on the adsorption of Malachite green

The effect of sodium chloride on the adsorption of Malachite green on *Terminalia Catappa Linn* carbon is shown in Fig. 7. In a low solution concentration NaCl had little influence on the adsorption capacity. At higher ionic strength the adsorption Malachite green will be 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 enhances adsorption of Malachite green ion onto *Terminalia Catappa Linn* carbon by pairing of their charges and hence reducing the repulsion between the Malachite green molecules adsorbed on the surface. This initiates carbon to adsorb more of positive Malachite green ions [1,17,18].

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 held by the adsorbent through chemisorption. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 82% 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 acid indicates that the dyes were adsorbed onto the activated carbon through by physisorption mechanisms [12,18,19].

CONCLUSION

Terminalia Catappa Linn plant has been available in different parts of the country. In the present study, *Terminalia Catappa Linn* carbon 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 >92% of dye removal was achieved by using 0.05 g of *Terminalia Catappa Linn* carbon. The kinetics of adsorption developed can be used to achieve low levels of dye from aqueous solutions utilizing *Terminalia Catappa Linn* carbon. Almost 95% removal of dye was observed at pH of 9.5. The adsorption data seems to follow the Langmuir and Freundlich isotherms.

REFERENCES

[1] Arivoli, S. Kinetic and thermodynamic studies on the adsorption of some metal ions and dyes onto low cost activated carbons, Ph D., Thesis, Gandhigram Rural University, Gandhigram**, 2007**.

[2] Sekaran, G.; Shanmugasundaram, K. A.; Mariappan, M.; Raghavan, K. V. *Indian J. Chem. Technol.***,** **1995**, 2, 311**.**

[3] Selvarani, K. Studies on Low cost Adsorbents for the removal of organic and Inorganics from Water**,** Ph D., Thesis, Regional Engineering College, Tiruchirapalli, **2000**.

[4] Jia, Y. F.; Thomas, K. K. Adsorption of metal ion on nitrogen surface functional groups in activated carbon, *Langmuir,* **2002**, 18, 470.

[5] Namasivayam, C.; Muniasamy, N.; Gayathri, K.; Rani, M.; Renganathan, K. *Biores. Technol.*, **1996**, 57, 37.

[6] Namasivayam, C.; Yamuna, R. T. *Environ. Pollut.,* **1995**, 89, 1.

[7] Langmuir, I., *J. Amer. Chem. Soc.,* **1918**, 40, 1361.

[8] Freundlich, H. *Phys. Chemie.*, **1906**, 57, 384.

[9] Krishna, D. G.; Bhattacharyya, G., *Appl. Clay Sci.,* **2002**, 20, 295.

[10] Arivoli, S.; Viji Jain, M.; Rajachandrasekar, T. *Mat. Sci. Res. India,* **2006,** 3, 241-250.

[11] Arivoli, S.; Hema, M., *Intern. J. Phys. Sci.,* **2007,** 2, 10.

[12] Arivoli, S.; Venkatraman, B. R.; Rajachandrasekar, T.; Hema, M., *Res. J. Chem. Environ.*, **2007**, 17, 70.

[13] Arivoli, S.; Kalpana, K.; Sudha, R.; Rajachandrasekar, T., *E. J. Chem.,* **2007**, 4, 238.

[14] Renmin Gong, Yingzhi Sun, Jian Chen, Huijun Liu, Chao yang, *Dyes and Pigments***, 2005**, 67, 179.

[15] Vadivelan, V.; Vasanthkumar, K., *J. Colloid Interf. Sci.,* **2005,** 286, 91.

[16] Weber, W. J. Principle and Application of Water Chemistry, edited by Faust, S. D.; Hunter, J. V., Wiley, New York, **1967**.

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

[18] Yupeng Guo, Jingzhu Zhao, Hui Zhang, Shaofeng Yang, Zichen Wang and Hongding Xu,, *Dyes and Pigments,* **2005**, 66, 123.

[19] Sreedhar M K and Anirudhan T S**,** *Indian J. Environ. Protect.***, 1999**, 19, 8.