Jr. of Industrial Pollution Control 27(1)(2011) pp 5-13

ADSORPTION KINETICS AND THERMODYNAMICS OF MALACHITE GREEN DYE ONTO *CALATROPIS GIGANTIS* BARK CARBON

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Key words : Adsorption, *Calatropis gigantis* bark carbon, Kinetics and thermodynamics, Other ions.

ABSTRACT

The removal of toxic dye such as malachite green from waste water by adsorption using activated carbons received much interest. However, the success of this approach depends on economic feasibility, which can be obtained by optimization of the environmental conditions. This paper evaluates the use of low cost *Calatropis gigantis* bark carbon to eliminate malachite green from aqueous solutions. The effect of some parameters studied shows that the maximum sorption capacity was reached within 40 minutes. The adsorption followed first order reaction equation and the rate is mainly controlled by intra-particle diffusion. The temperature variation study showed that the malachite green adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the malachite green solutions. The Langmuir and Freundlich adsorption isotherms obtained, positive êH0 value, pH dependent results and desorption of malachite green in mineral acid suggest that the adsorption of malachite green on *Calatropis gigantis* bark carbon involves physisorption mechanism.

INTRODUCTION

The discharge of highly coloured effluents into natural water bodies is not only aesthetically displeasing, but it also impedes light penetration, thus upsetting biological processes within a stream. In addition, many dyes are toxic to some organisms causing direct destruction of aquatic communities. Some dyes can cause allergic dermatitis, skin irrigation, cancer and mutation in man. Recent estimates indicate that, approximately, 12% of synthetic textile dyes used each year lost during manufacture and processing operation and 20% of these dyes enter the environment through effluents that result from the treatment of residual industrial waters. Wastewaters from dyeing industries released in to nearby land or rivers without any treatment because the conventional treatment methods are not cost effective in the Indian context. Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed to treat wastewater containing different classes of dyes, recognizing the economic drawback of commercial activated carbon.

Many investigators have studied the feasibility

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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 (Arivoli, 2007; Sekaran *et al.* 1995 and Selvarani, 2000).

The present study was undertaken to evaluate the efficiency of a carbon adsorbent prepared from acid activated *Calatropis gigantis* bark carbon for the 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 was reported.

EXPERIMENTAL APPROACHES

Materials

Adsorbent Materials

The dried *Calatropis gigantis* bark was carbonized with concentrated sulphuric acid in the weight ratio of 1:1 (w/v). The resulting carbon was washed with distilled water until a constant pH of the slurry was reached. Then the carbon was dried for four hours at 100°C in a hot air oven. Heating for twelve hours in a furnace at 600°C has completed the activation.. 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 10 mg/L to 50 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 10 to 50 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^o 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.

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 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 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	CGC
Particle size (mm)	0.048
Density (g/cc)	0.2876
Moisture content (%)	2.50
Loss on ignition (%)	89
Acid insoluble matter (%)	1.75
Water soluble matter (%)	0.73
pH of aqueous solution	6.5
pHzpc	6.1

Effect of contact time and initial dye concentration

The experimental results of adsorptions of at various concentrations (10 to 50 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 (Namasivayam *et al.* 1996 and Namasivayam and Yamuna, 1995). 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.

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 30 mg/L of dye concentration. The percent adsorption increased with increase in the carbon concentration (Figure 2). This was attributed to increased carbon surface area and availability of more adsorption sites (Namasivayam *et al.* 1996 and Namasivayam and Yamuna, 1995). Hence the entire studies are carried out with the adsorbent dose of 25 mg of adsorbent /50 mL of the adsorbate solution.

Adsorption isotherm

Fig. 1 shows the Langmuir adsorption (Jia and Thomas, 2002) isotherms of the dye at 303, 313, 323 and 333 K using the Calatropis gigantis bark Carbon (CGC). The Langmuir equation assumes 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 (Freundlich, 1906) model is generally found to be better suited for characterizing multi-layer adsorption process. The Langmuir parameters, Qm and b were computed from the slopes and intercepts of the straight lines of plot of Ce/Qe vs. Ce (Figure.3), while the values of Freundlich constants, i.e. Kf and 1/n were calculated from the plots (Figure 4) of log Qe against log Ce. Qm and b are Langmuir constants related to absorption capacity and energy of adsorption, respectively, while Kf indicates the adsorption capacity and 1/n is indicative of the intensity of reaction (Krishna and Bhattacharyya, 2002 ; Arivoli *et al.* 2006 and Arivoli and Hema , 2007). Parameters of the Langmuir and Freundlich isotherms are compiled in Table 3 and 4, the essential characteristics of a Langmuir constant is the equilibrium parameter, RL,

$$RL = 1/\ (1+bCo)$$

Where b is Langmuir constant and Ce is the initial concentration of the dye (Arivoli *et al.* 2006 and Arivoli and Hema , 2007). The value of RL, calculated from the above expression shown in Table 5, indicates favourable adsorption of malachite green oxalate on *Calatropis gigantis* bark 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 (ΔG°) (J/mol), enthalpy (ΔH°)(kJ/mol) and entropy (ΔS°)(J/K/mol) were determined using the following equations

$$K0 = C_{solid}/C_{liquid}$$

$$\Delta G° = -RT \ln K_O$$

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

Where Ko is the equilibrium constant, Csolid is the solid phase concentration at equilibrium (mg/L), Cliquid is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin and R is the gas constant. The ΔH° and ΔS° values obtained from the slope and intercept of Van't Hoff plots have presented in Table 6.

The values of ΔH° and ΔS° and ΔG° were calculated as previously. Positive values of ΔH° and ΔS° suggest endothermic reaction, while the negative values of free energy change (ΔG°) indicate that the adsorption is spontaneous (Table 6) .The positive values of ΔS° suggest the increased randomness at the solid-solution interface during desorption of malachite green oxalate on *Calatropis gigantis* bark 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 (Arivoli and Hema, 2007; Arivoli *et al.* 2007; Arivoli *et al.* 2007 and Renmin Gong, *et al.* 2005).

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

$$B \underset{k2}{\overset{k1}{\rightleftarrows}} A$$

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 (Arivoli , 2007).

$$\log C0/C_t = (K_{ad}/2.303)t$$

Where C_0 and Ct 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

$$K_{ad} = k_1 + k_2 = k_1 + (k_1/K_0) = k_1[1+1/K0]$$

The overall rate constant kad 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 (kad) increases with increase in temperature suggesting that the adsorption process in endothermic in nature. Further, kad 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 (Arivoli , 2007; Arivoli and Hema, 2007 and Arivoli *et al.* 2007).

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, 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.

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

[MG]0	Ce (mg/L)				Qe (mg/g) Temperature (°C)				Dye removed (%)			
	30°	40°	50°	60°	30°	40°	50°	60°	30°	40°	50°	60°
10	1.4415	1.1402	0.9505	0.8015	17.117	17.7196	18.099	18.3970	85.58	88.59	90.49	91.98
20	3.7545	3.5162	3.3092	3.1156	32.491	32.9676	33.3816	33.7688	81.22	82.41	83.45	84.42
30	7.2415	7.0012	6.8015	6.6012	45.517	45.9976	46.3970	46.7976	75.86	76.66	77.32	77.99
40	12.5814	12.0146	11.5177	11.0185	54.8372	55.9708	56.9646	57.9630	68.54	69.96	71.20	72.45
50	20.4056	19.5165	18.6189	17.7950	59.1888	60.967	62.7622	64.4100	59.18	60.96	62.76	64.41

Table 3. Langmuir isotherm results

Dye	Temp	Statistical parameters/constants		
	⁰C	r^2	Q_m	b
MG	30	0.9932	72.99	0.2197
	40	0.9908	73.52	0.2531
	50	0.9965	74.62	0.2754
	60	0.9946	75.75	0.2967

Table 4. Freundlich isotherm results

Dye	Temp	Statistical parameters/constants		
	⁰C	r^2	K_f	n
MG	30	0.9964	3.3267	2.1027
	40	0.9868	3.4952	2.2391
	50	0.9905	3.6171	2.3288
	60	0.9952	3.7281	2.4102

Table 5. Dimensionless Separation factor (RL)

	Temperature (⁰C)			
[MG]0 (mg/L)	30	40	50	60
10	0.312	0.283	0.266	0.252
20	0.185	0.165	0.153	0.144
30	0.132	0.117	0.108	0.101
40	0.102	0.089	0.083	0.077
50	0.083	0.073	0.067	0.063

The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds by surface sorption and intraparticle diffusion (Vadivelan *et al.* 2005 and Weber, 1967). 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

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

[MG]0	K_0				ΔG° Temperature (^{0}C)					
	30°	40°	50°	60°	30°	40°	50°	60°	ΔH°	ΔS°
10	5.937	7.770	9.520	11.476	-4487.20	-5335.51	-6051.54	-6756.15	18.32	75.41
20	4.326	4.687	5.043	5.419	-3690.19	-4020.52	-4345.42	-4678.78	6.27	32.90
30	3.142	3.284	3.410	3.544	-2884.70	-3095.05	-3294.86	-3503.43	3.34	20.56
40	2.179	2.329	2.472	2.630	-1962.42	-2200.39	-2431.38	-2677.43	5.23	23.75
50	1.450	1.561	1.685	1.809	-936.55	-1160.42	-1401.87	-1642.32	6.21	23.56

Table 7. Rate constants for the adsorption of Malachite green dye (kad, min -1) and the constants for forward (k_1, min $^{-1}$) and reverse (k2, min-1) process

	Temperature (^{0}C)											
$[D]_0$	k_{ad}				30		40		50		60	
	30°	40°	50°	60°	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2
10	0.0236	0.0194	0.0158	0.0128	0.0202	0.0034	0.0157	0.0036	0.0120	0.0038	0.0087	0.0040
20	0.0274	0.0203	0.0141	0.0133	0.0242	0.0031	0.0167	0.0035	0.0108	0.0032	0.0093	0.0040
30	0.0271	0.0215	0.0167	0.0138	0.0245	0.0025	0.0180	0.0035	0.0129	0.0037	0.0098	0.0039
40	0.0345	0.0249	0.0172	0.0139	0.0317	0.0027	0.0210	0.0038	0.0134	0.0037	0.0101	0.0038
50	0.0415	0.0284	0.0184	0.0141	0.0389	0.0025	0.0247	0.0037	0.0145	0.0038	0.0112	0.0029

of the surface sorption in the rate limiting step. The calculated intraparticle diffusion coefficient K_p value was given by 0.525, 0.559, 0.591, 0.635 and 0.677 mg/g min$^{0.5}$ for initial dye concentration of 10, 20, 30, 40 and 50 mg/L at 30^{0}C.

Effect of pH

The influence of pH on the dye adsorption onto *Calatropis gigantis* bark carbon was studied while the dye concentration, shaking time and amount of adsorbent were fixed. The variation of malachite green adsorption on *Calatropis gigantis* bark Carbon over a pH range of 2.0-10.0 is shown in Fig. 6. The result reveals that the adsorption of the dye increases from 48% to 92% with an increase in pH of the solution from 2.0 to 9.0 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 *Calatropis gigantis* bark Carbon was 6.1. 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 9.0. 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 (Tahir and Naseem, 2006;Yupeng Guo,*et al.* 2005 and Sreedhar and Anirudhan , 1999).

Effect of the ionic strength on the adsorption of Malachite green

The effect of sodium chloride on the adsorption of Malachite green on CGC 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 CGC 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 (Arivoli , 2007; Tahir and Naseem Rauf, 2006 and Yupeng Guo, *et al.* 2005).

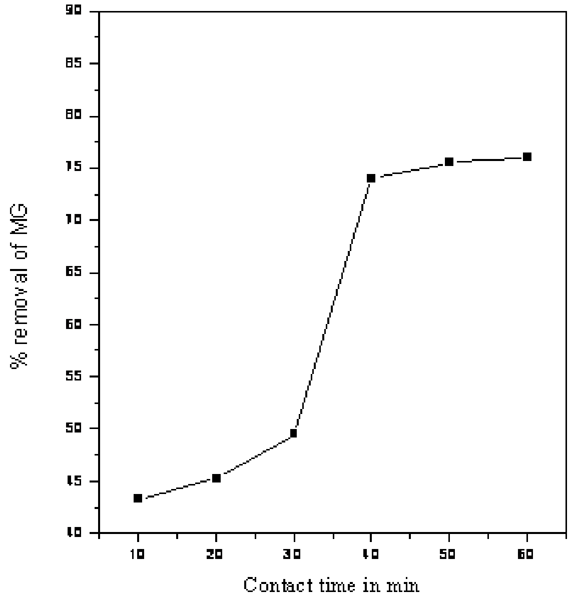

Fig. 1 Effect of contact time on the adsorption of malachite green [MG] = 30 mg/L; Adsorbent dose = 25 mg/50mL

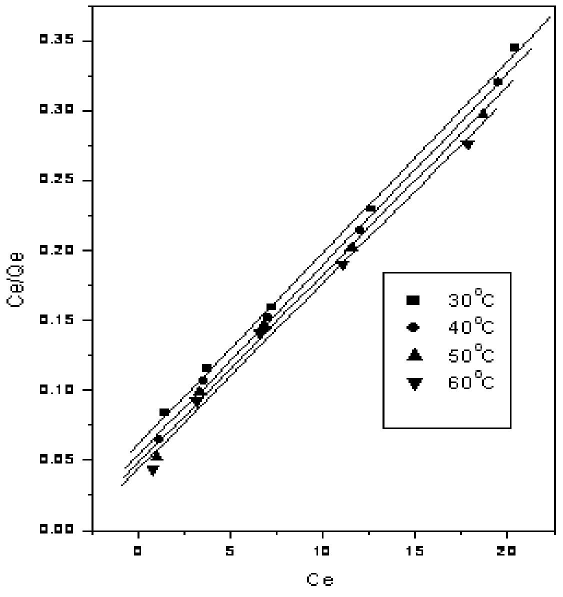

Fig. 3 Linear Langmuir Isotherm for the adsorption of MG

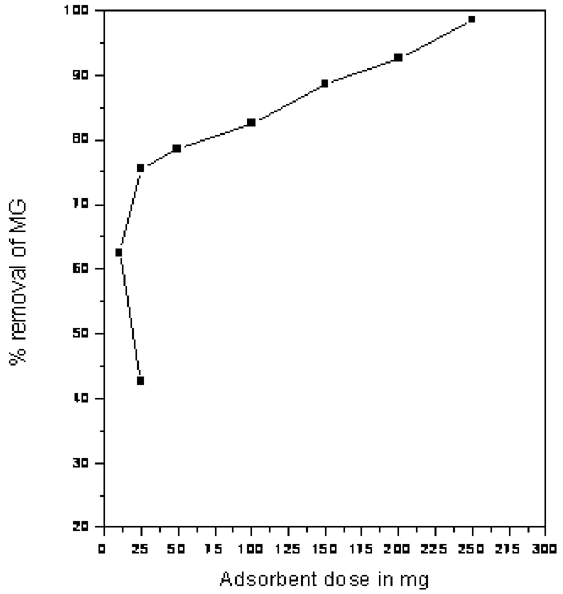

Fig. 2 Effect of adsorbent dose on the of adsorption malachite green [MG] = 30 mg/L; Contact time = 60 min

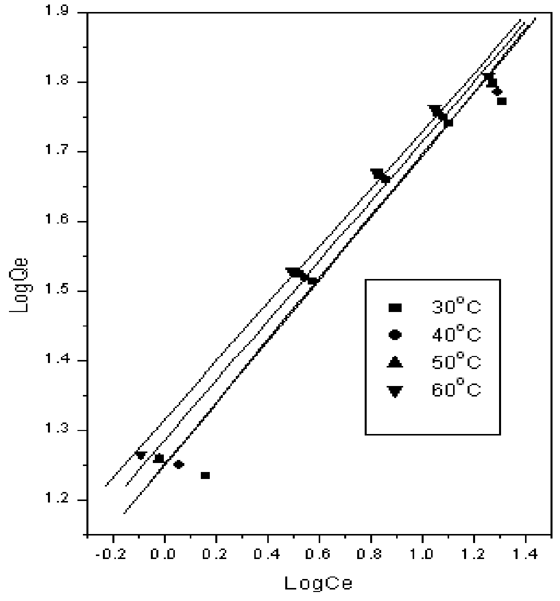

Fig. 4 Linear Freundlich Isotherm for the adsorption of MG

Desorption studies

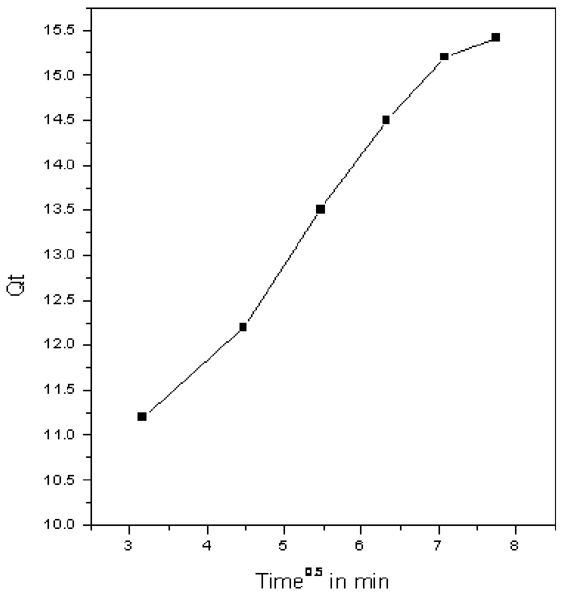

Fig. 5 Intraparticle diffusion effect for the adsorption of malachite green dye [MG] = 30 mg/L; Contact time = 60 min; Adsorbent dose = 25 mg/50 mL

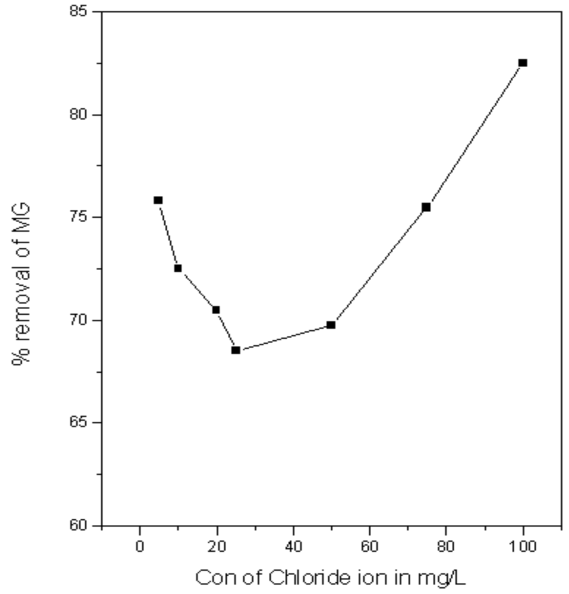

Fig. 5 Effect of other ions on the adsorption of malachite green [MG] = 30 mg/L; Contact time = 60 min; Adsorbent dose = 25 mg/50 mL

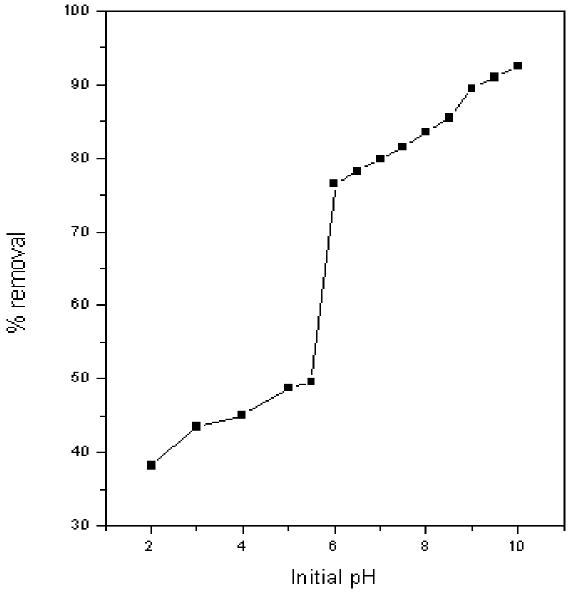

Fig. 5 Effect of pH on the adsorption of malachite green [MG] = 30 mg/L; Contact time = 60 min; Adsorbent dose = 25 mg/50 mL

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 73% 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 indicates that the dyes were adsorbed onto the activated carbon through by physisorption mechanisms (Arivoli *et al.* 2007; Yupeng Guo, *et al.* 2005 and Sreedhar and Anirudhan, 1999).

CONCLUSION

Calatropis gigantis bark Carbon has been available in different parts of the country. In the present study, *Calatropis gigantis* bark 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 >81% of dye removal was achieved by using 0.025 g of Calatropis gigantis bark Carbon. The kinetics of adsorption developed can be used to achieve low levels of dye from aqueous solutions utilizing. Almost 82% removal of dye was observed at pH of 8.0. The adsorption data seems to follow the Langmuir and Freundlich isotherms.

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