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Plant waste - Economical adsorbent for the removal of cationic dye from aqueous solution

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ABSTRACT

Removal of Malachite Green (MG) dye in aqueous solution on Osimum Sanctum Carbon (OSC) has been studied at 30 ± 1°C. The effect of various experimental parameters has been investigated using a Batch Adsorption technique (BAT) to obtain information on treating effluents from the dye industry. The percentage removal was found to increase with decrease in initial concentration of dye and increase in contact time and dose of adsorbent. The dye adsorption is found to be pH sensitive. The percentage removal increases with increase in initial pH for MG. Adsorption data were modeled using the Freundlich and Langmuir adsorption isotherms and first order kinetic equations. The kinetics of adsorption was found to be first order with regard to intra-particle diffusion as the rate determining step. The results indicate that OSC is one of the best adsorbent that can be used in wastewater treatment for the removal of colors and dyes.

Keywords: Adsorption of Malachite Green dye, Batch Adsorption technique, Osimum *Sanctum* Bark , adsorption isotherms, Kinetics of adsorption.

INTRODUCTION

Now a days, the increase of industrial activities have intensified problems in environmental pollution and the deterioration of several ecosystems with the accumulation of pollutants, especially dyes. Effluents containing dyes and heavy metals are discharged from various industrial processes.Water pollution is a very persistent problem; the intensive disposal of different toxic substances without control constitutes a real danger. Wastewaters from the textile, cosmetics, printing, dyeing, food colouring, paper making etc., are polluted by dyes. Most of the dyes are stable to biological degradation. Coloured waters are often objectionable an aesthetic grounds for drinking and other agricultural purposes. Color affects the nature of water by inhibiting sunlight penetration, thus reducing photosynthetic action. Some dyes are carcinogenic and mutagenic [1]. Therefore, there is a considerable need to treat such element prior to discharge. Most of the used dyes are stable to photo degradation, Bio-degradation and Oxidizing agent [2].

The wastewater from the dye industry has substantial amount of colouring materials or dyestuffs. These substances will pollute the drinking water, when they are discharged into river without any pretreatment

and also affect the aquatic life. Hence it is imperative that the removal of these coloured matters from the effluents of dye industries is highly essential, however, many processes were made in order to remove the colouring matter from water and wastewater using the adsorption technique. The adsorption process is one of the efficient methods to remove dyes from effluent [3].

The adsorption process has an advantage over the other methods due to the excellent adsorption efficiency of activated carbon. It over comes the problem of the water treatment techniques[4] by taking advantage of an adsorbent's surface having an affinity for a particular molecular or ionic species coming onto contact with it. A further benefit is that adsorption can be very simple and offers sludge free operation. The evaluation of activated carbon for color removal has been extensive [5] and effluent treatment systems using activated carbon have been successful. Some works of low cost, non-conventional adsorbents have been carried out which include, bananapith [6], sawdust [7], babulseed [8],fly ash [9], *Emblica Officinalis Bark* Carbon[10], m*oringa oliefera* bark [11], hen feathers [12], zea mays dust carbon [13] and tamarind seed powder [14] have also been reported as efficient adsorbent for removing colour.

MATERIALS AND METHODS

Chemicals and Adsorbent: Raw materials for the preparation of carbon such *Osimum Sanctum* Bark Carbon (OSC) were collected locally, washed, dried, cut into small pieces, carbonized (at 300 °C) and steam digested (at 900 °C) acid treated and washed. The materials were then sieved to discrete particle sizes and dried at 120 °C for 5 h in an air oven. Malachite Green (MG) supplied by BDH (India) was used as an adsorbate. All the other chemicals used in this study were of reagent grade and obtained commercially. Double distilled water was employed for preparing all the solutions and reagents. Adsorption data of the replicates (with in ± 1%) were reported.

Adsorption Experiments: Adsorption experiments were carried out literacy method. The various experimental conditions are given in table 1. The values of percentage removal of dye and amount adsorbed (q in mg g^{-1}) were calculated using the following relationships [15].

Percentage removal $= 100\ (C_i - C_e)/C_i$ ----------(1)

Aumont adsorbed (q) $= (C_i - C_e)/m$ ----------(2)

Where C_i and C_e are the initial and equilibrium (final) concentration of dye (in mgL^{-1}), respectively and m is the mass of adsorbent, in gL^{-1}.

RESULTS AND DISCUSSION

Effect of Initial Concentration: The effect of initial concentration of dye on the extent of removal of MG on OSC is studied at30 ± 1°C. The percentage removal decreased with the increase in initial concentration of MG (Fig.1). This indicates that the formation of monolayer of dye molecules on the surface of Adsorbent (OSC) and the formation of second layer of dye molecules is highly hindered at higher initial concentration of MG, due to repulsive interaction between adsorbed and unadsorbed dye molecules present on solid surface and in solution respectively [16].

Table 1: Effect of various parameters for the removal of MG by OSC at 30 ±1°C

S.No	Parameters	Variation (in range)	% removal of dye	Amount Adsorbed (q)
1	Initial concentration (ppm)	250-475 (375)*	99.7 - 91.6	24.95-33.73
2	Contact time (in min)	5-50	92.2 - 99.6	2155-32.56
3	Dose (gL^{-1})	150-240 (200)*	90.8 - 99.3	25.94-34.75
4	pH	2-11	89.6 - 96.7	26.23 -21.78
5	Particle size variation (Micron)	45-280	96.2 - 84.8	34.28-21.45

*****Optimum Initial Concentration

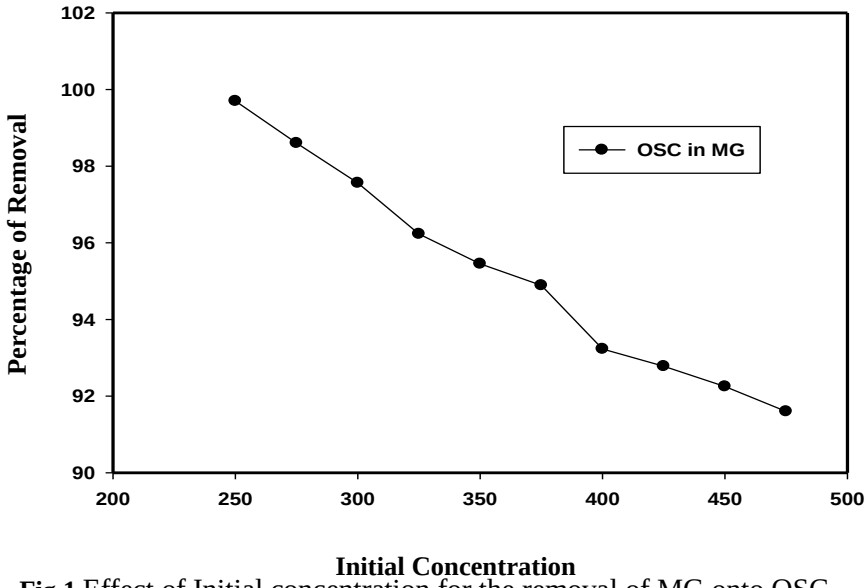

Fig.1 Effect of Initial concentration for the removal of MG onto OSC

Adsorption Isotherms: The study of adsorption has been of great importance and significance in the treatment of water and waste water by adsorption principle in selecting an adsorbent for the removal of dyes [17].The adsorption data for the removal of dyes on OSC at 30 ±1°Cwere used to fit the Freundlich and Langmuir isotherms.

Freundlich isotherms: $\log q_e = \log k + (1/n) \log C_e$ ---------- (3)

Langmuir isothermes : $(C_e/q_e) = (1/Q_o\, b) + (C_e/Q_o)$ ---------- (4)

Where, k and 1/n are the measures of adsorption capacity and intensity of adsorption, respectively. q is the amount dye adsorbed per unit mass of adsorbent(in mgg^{-1}) and C_e is the equilibrium concentration of dye (in mg L^{-1} or ppm); Q_o and b are the adsorption capacity(in mg g^{-1}) and b is the Langmuir constant, which are the measures of monolayer adsorption capacity(in mgg^{-1}) and surface energy (in g L^{-1}), respectively. In order to compare the validity of each isotherm models more efficiently, a normalized standard deviation, Δq (%) is calculated using the following equation [18]:

$$\Delta q\ (\%) = 100 \times [(\sum[(q_t^{exp.} - q_t^{cal.})/q_t^{exp.}]^2)/\ (n - 1)]^{1/2} \quad \text{----------} \quad (5)$$

where the superscripts, exp. and cal. are the experimental and calculated values of q_t,the amount adsorbed at different time t and n is the number of measurements. The Δq (%) values are also given in table 2. Based on the low values of Δq (%), it is concluded that the adsorption of MG can best be described by the Freundlich adsorption isotherm. Freundlich adsorption isotherm plots are shown in Fig.2. Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following equation [19].

$$R_L = [1 / (1 + bC_i)] \quad \text{----------} \quad (6)$$

Where, $R_L$is the separation factor, C_i and b are the initial concentration of dye (in mg L^{-1} or in ppm) and Langmuir constant (in g L^{-1}). The value of R_L, indicates the shape of the isotherm and nature of the adsorption process as given below;

R_L value	Nature of adsorption process
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

In the present study, the value of R_L (0.006) indicates that the adsorption process is favorable for this low-cost adsorbent.

Table 2. Adsorption Isotherm for the removal of MG by OSC at 30±1^0 C

S. No	Parameters	Adsorbent (OSC)
1	**Freundlich isotherm**	
	Slope (1/n)	0.103
	Intercept (log k)	1.423
	Slope (1/n)	0.103
	Correlation Coefficient (r)	0.984
	Δq %	0.325
2	**Langmuir isotherm**	
	Slope ($1/Q_0$)	0.027
	Intercept ($1/Q_0b$)	0.022
	Correlation Coefficient (r)	0.994
	Q_0(mg g^{-1})	36.49
	b (gL^{-1})	1.274
	R_L	0.006
	Δq %	2.256

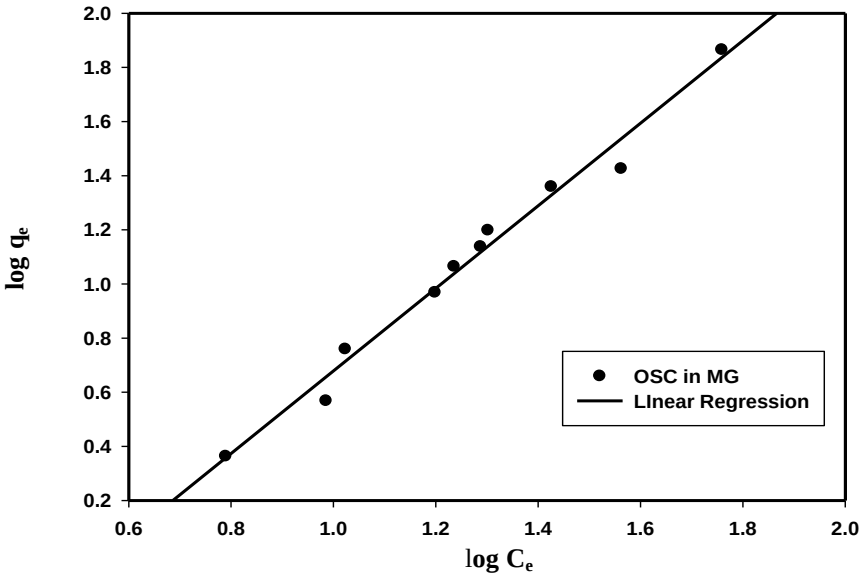

Fig 2. Freundlich adsorption isotherm for the removal of MG onto OSC

Effect of Contact Time: In order to study, the effect of contact time on the removal of MG by adsorption on OSC was studied at constant dose of adsorbent and optimum initial concentration of dye at 30 ±1°C(Table1).The values of percentage removal and amount of MG adsorbed exponentially increase with the increase in contact time (Fig.3) [20].

The mechanism of the removal of dyes by adsorption on various adsorbents from aqueous solution may be assumed to involve the following 4 steps [21]: a) Migration of dye from the bulk of the solution to the surface of the boundary layer to the surface of the adsorbent, b) Diffusion through the boundary layer to the surface of the adsorbent, c) Adsorption at an active site on the surface of adsorbent and d) Intra-particle diffusion into the interior pores of the adsorbent particle.

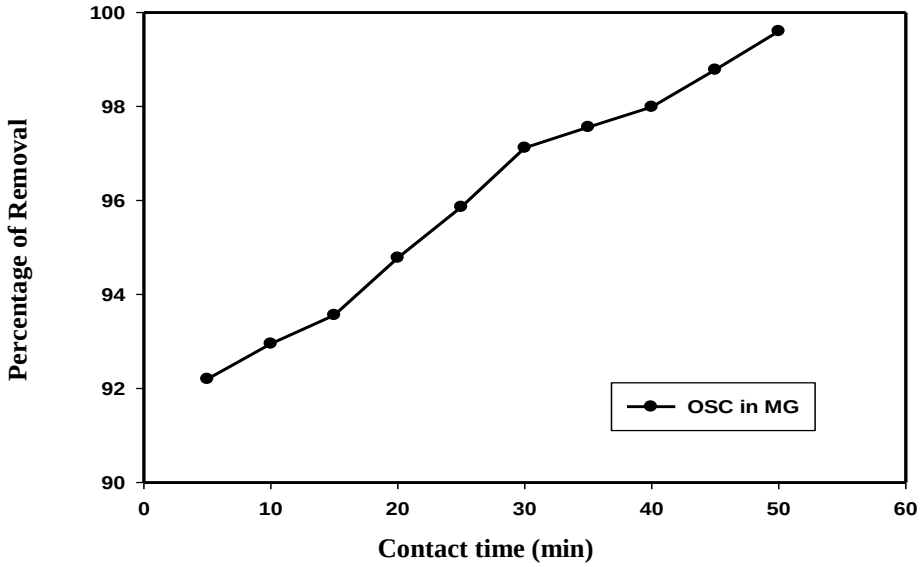

Fig. 3 Effect of contact time for the extent removal of MG

Kinetics of Adsorption: The following kinetics equations were employed to study the kinetics and dynamics of adsorption of dyes under the condition of first order kinetics [22].

Natarajan and Khalaf equation : $\text{Log } [C_i / C_t] = (k / 2.303)\ t$ ---------- (6)

Lagergren's equation : $\text{Log } (q_e - q_t) = \text{Log } q_e - [k/2.303]$ ----- -- (7)

Bhattacharya and Venkobachar equation : $\text{Log } (1\text{-}U(T)) = -[k/2.303]\ t$ -------- (8)

Where C_i and C_t are the concentration of dye (in mg L^{-1}), at time Zero (initial concentration) and at time t respectively; q_e and q_t are the amount of dye adsorbed per unit mass of the adsorbent (in mg g^{-1}) and at time t respectively, $U(T) = (C_i - C_t) / (C_i - C_e)$, C_e is equilibrium dye concentration (in mg L^{-1}) and k and k are the first order adsorption rate constants (in min^{-1}). The values of Log (C_i / C_t), Log (q_e / q_t) and Log (1-U (T)) were correlated with time (in min) and the kinetic plots are found to be linear Legergren plots are shown in figure 4. These values are to each other as evidenced from the values of correlation coefficients (r values) close to unity (Table3). The results indicate the applicability of these kinetic equations and first order nature of the adsorption kinetics. The k values calculated from Legergren equation are found to be close to that obtained from Bhattacharya –Venkobachar equation. The values of first order rate constants along with the correlation coefficients are given in table 3. The maximum and minimum k values are noted for adsorbent 9.598 $x10^{-2} min^{-1}$ and 9.305 x 10^{-2} min^{-1}, respectively.

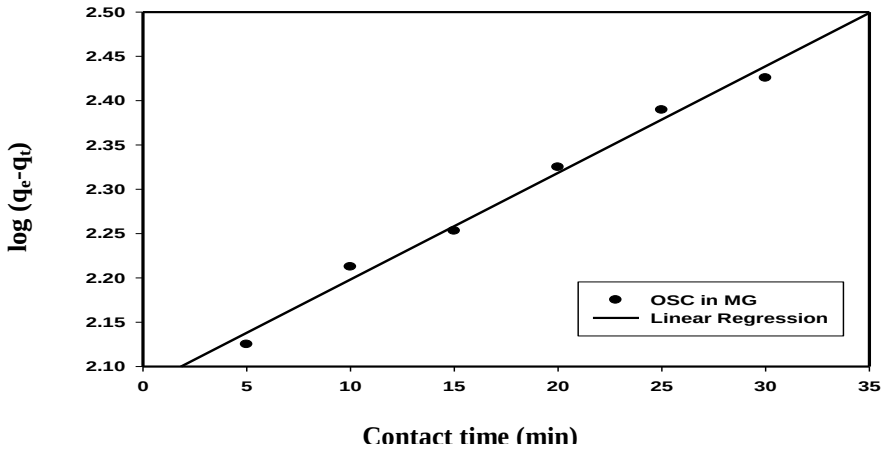

Fig. 4 Legergren Plots for the removal of MG onto OSC at 30±1°C

Intra-Particle Diffusion Model: The adsorbate (MG) species are most probably transported from the bulk of the solution to the solid phase through intra-particle diffusion/transport process, which is often rate limiting step in many adsorption processes, especially in a rapidly stirred batch reactor. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model [23].

$$q_t = k_p t^{½} + C \quad \text{---------} \quad (9)$$

Where q_t is the amount of dye adsorbed (in mg g^{-1}) at time t; C is the intercept and k_p is the intra- particle diffusion rate constant (in mg g^{-1} $min^{-½}$). The values of q_t were found to be linearly correlated with values of $t^{-½}$, the k_p values are calculated and given in table (3).The results indicate the presence of intra-particle diffusion process as rate determining step. The values of intercept (C) give an idea about the boundary layer thickness that is, the larger the intercept, the greater is the boundary layer effect [24].

The correlation of the values of log (% removal) and log (time) also resulted in linear relationship. This indicates that the process of intra particle diffusion is also taking place in these adsorption systems (Table 3). The value of slope (0.214) indicates the presence of intra particle diffusion process as one of the rate limiting steps, besides many other processes controlling the rate of adsorption, all of which may be operating simultaneously [25].

Table 3. Kinetics and dynamics of adsorption of MG by adsorption on OSC at 30 ±1°C.

S. No	Parameters	OSC
01	**Natarajan & Khalaf equation.**	
	Correlation Coefficient (r)	0.974
	10^2k (min^{-1})	9.395
	Δq (%)	34.25
02	**Lagergren equation.**	
	Correlation Coefficient (r)	0.986
	10^2k (min^{-1})	9.598
	Δq (%)	4.035
03	**Bhattacharya and Venkobachar equation.**	
	Correlation Coefficient (r)	0.983
	10^2k (min^{-1})	9.305
	Δq (%)	12.18
04	**Intra Particle diffusion Model.**	
	Correlation Coefficient (r)	0.986
	k_p(mg g^{-1} $min^{-1/2}$)	0.396
	Intercept (C)	2.369
	Δq (%)	0.039
05	**Log (% removal) Vs log (time)**	
	Correlation Coefficient (r)	0.936
	Slope (m)	0.214
	Δq(%)	38.04

Effect of Dose of Adsorbent: The effect of dose of adsorbent on the Adsorption of MG was studied by varying the dose of adsorbent (Table.1).The percentage removal of dye by adsorption on OSC increases with the increase of dose of OSC (Fig.5) This is due to the increase in the availability of the active sites on the surface of the adsorbent, this may also be due to the increase in the effective surface area resulting from the conglomeration of the adsorbent especially at higher dosage of adsorbent [26]. The optimum dose of OSC was fixed as 2 gL^{-1} for MG. The values of percentage of removal were found to be maximum (OSC=99.3%) at the optimum dose of OSC (4 gL^{-1}).

Effect of Initial pH: The effect of initial pH of the dye solution on the amount of dye adsorbed was studied by varying initial pH of dye solution and keeping the other process parameters as constant. The increase in initial pH of the dye solution increased the amount of dye solution adsorbed (Fig.6). This result is in harmony with the literature reports [27], the final pH of the dye (MG) solution after adsorption was found be increases, due to adsorption of the basic form of dye molecule.

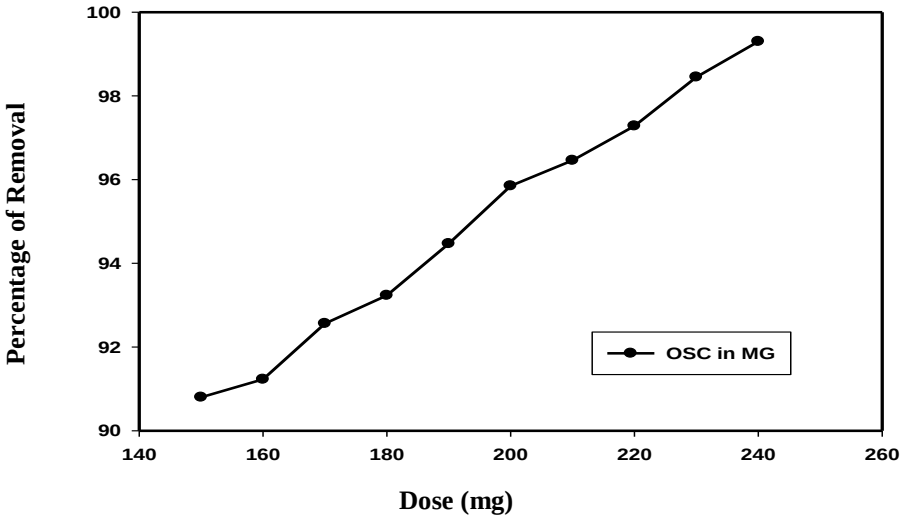

Fig. 5 Effect of dose for the removal of MG onto OSC

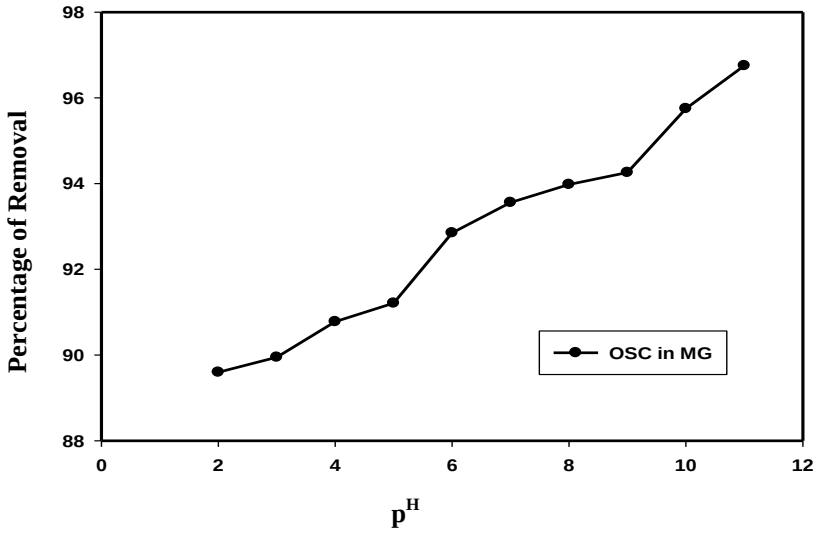

Fig. 6 Effect of initial pH for the removal of MG onto OSC

Effect of Particle Size: The effect of particle size on the percentage removal of MG adsorbed is given in the Table.1. The effect of particle size on the percentage removal of MG dye adsorbed was studied only by varying the particle size of OSC such as 45, 90,125..... 280 microns the amount of MG adsorbed increases with decrease in particle size of the adsorbent (Fig.7). This is due to the increase in the availability surface area with the decrease in particle size [28].

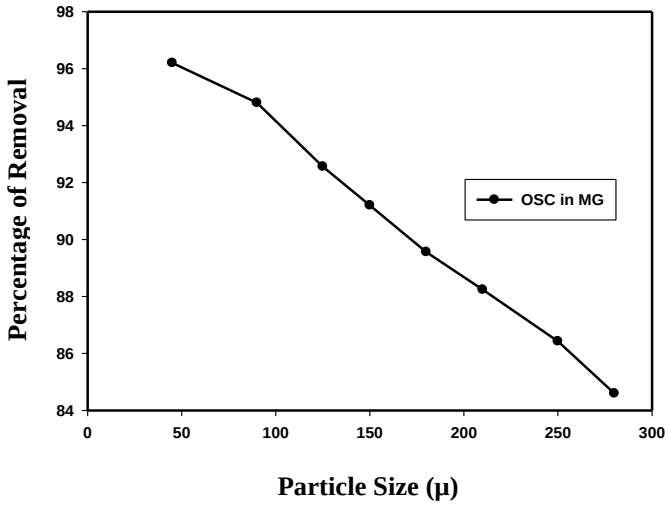

Fig. 7 Effect of Particle size for the removal of MG onto OSC

APPLICATIONS

The adsorption kinetics data may be useful in construction, designing and fabrication of an economic treatment plant for the removal of Malachite Green dye from wastewater.

CONCLUSIONS

The conclusions derived from the present investigation are the percentage of removal of MG increased with decrease in initial concentration of dye, particle size of the adsorbent and increases in contact time, dose of adsorbent and initial pH of the dye solution. Adsorbate species are found to adsorb strongly on the surface of *Osimum Sanctum* Carbon. The adsorption is found to be first order with intra-particle diffusion as one of the rate determining steps. OSC could be considered as cost-effective adsorbent and it is highly useful for the economic treatment of waste water containing Malachite Green dye. The adsorption kinetics data may be useful in construction, designing and fabrication of an economic treatment plant for the removal of Malachite Green dye from wastewater.

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