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Research Article

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Removal of Basic Green Dye from Aqueous Media by using *Eucalyptus globules* Bark Carbon as an adsorbent-A comparative study

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ABSTRACT

Removal of Malachite Green (MG) in aqueous solution on Eucalyptus Globules Bark Carbon (EGBC) has been studied. 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 extent of dye removal increased with decrease in the initial concentration of the dye and increased with increase in contact time, amount of adsorbent used and the initial pH of the dye solution. 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 adsorption capacity of dye has been compared with CAC. These results indicate that EGBC 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, Batch Adsorption technique, *Eucalyptus Globules* Bark Carbon, adsorption isotherms, Kinetics of adsorption.

INTRODUCTION

Water pollution is a very persistent problem; the intensive disposal of different toxic substance without control constitutes a real danger. Wastewaters from the textile, cosmetics, printing, dyeing, food coloring, paper making, etc., are polluted by dyes. Most of the dyes are stable to biological degradation. Colored waters are often objectionable on aesthetic grounds for drinking and other agricultural purposes. Color affects the nature of water by inhibiting sunlight penetration, thus reducing photo synthetic action. Some dyes are carcinogenic and mutagenic [1,2].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 [3,4].Currently, several physical or chemical processes are used to treat dye-laden wastewaters. However, these processes are costly and cannot effectively be used to treat the wide range of dye wastewater. The adsorption process is one of the efficient methods to remove dyes from effluent [5,6].

The adsorption process has an advantage over the other methods due to the excellent adsorption efficiency of activated carbon [7]. It over comes the problem of the water treatment techniques[8] 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 [9] and effluent treatment systems using activated carbon have been successful. Some works of low cost, non-conventional adsorbents have been carried out which include, agricultural solid waste, Such as Coir pith [10], Banana pith [11],Coconut husk [12], Sawdust [13], Peat moss [14], Paddy straw [15], Nilgiri leaves[16] and industrial solid wastes such as fly ash , coal, Red mud ,Fe (III)/ Cr (III) hydroxide and Copper ion[17]. The objective of this present study is to explore the feasibility of using carbonized Eucalyptus globules bark carbon (EGBC) as an adsorbent for the removal of Malachite Green, which is most widely used in various textile-processing industries by varying parameters like Initial concentration, contact time, dose variation pH and particle size.

EXPERIMENTAL SECTION

Eucalyptus Globules Bark (EGB) 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 dried at 120°C for 5 hr in an air oven and then sieved to discrete particle sizes.

Basic Green Dye (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 [18],[19]. 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:

$$\textbf{Percentage removal} = 100\,(C_i - C_e)/C_i \qquad (1)$$

$$\textbf{Amount adsorbed (q)} = (C_i - C_e)/m \qquad (2)$$

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

The adsorption experiments were carried out at different experimental conditions (Table 1) and the results obtained are discussed below:

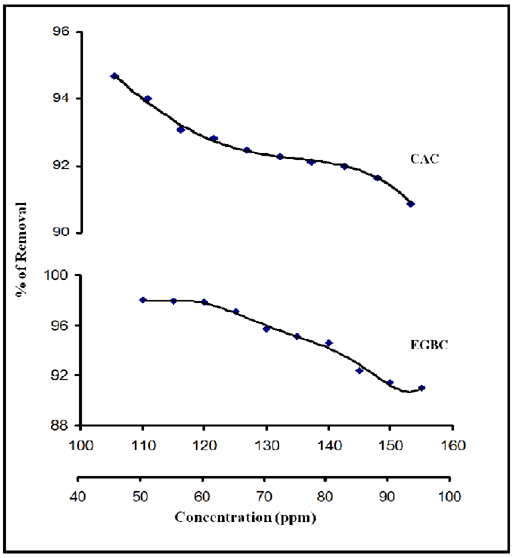

Figure -1 Effect of Initial concentration for the removal of MG onto CAC and EGBC.

Effect of initial concentration:

The effect of initial concentration of dye on the extent of removal of MG (in terms of percentage removal) on EGBC is studied at 30 ± 1°C is given in figure 1 and the relevant data are given in table 1. The percentage removal decreased with the increase in initial concentration of MG. This indicates that there exists a reduction in immediate solute (dye) adsorption, owing to the lack of available active sites required for the high initial concentration of MG. Similar results have been reported in literature on the extent of removal of dyes. Although, the adsorption capacities of low cost carbon (as revealed by Q_o values in table 2) is less, but still it could be considered as alternatives to CAC for the removal of dyes [20].

Table 1- Effect of process parameters on the extent of removal of MG by CAC and EGBC at 30 ±1°C

Process Parameters	Range		Percentage Removal (%)		Amount Adsorbed (in mg/L)	
	CAC	EGBC	CAC	EGBC	CAC	EGBC
Initial Conc.(ppm)	50-500	20-200	93.46-65.73	98.00-91.00	27.10-41.00	21.95-33.75
Contact time (min)	5-50	5-50	72.75-92.80	93.95-97.80	21.00-32.70	23.50-33.87
Dose of adsorbent (g/L)	1-2	3.5-4.4	82.60-93.20	64.28-93.67	21.86-35.30	22.95-29.70
Initial pH	2-11	2-11	98.70-92.80	93.25-76.20	22.25-17.78	32.78-23.58
Particle size (μ)	90-250	90-250	--	93.26-99.60	--	23.25-32.75

Adsorption Isotherms:

In order to determine the adsorption potential, the study of sorption isotherm is essential in selecting an adsorbent for the removal of dyes. [21].The adsorption data were analyzed with the help of Freundlich and Langmuir isotherms.

$$\textbf{Freundlich isotherms: } \log q = \log K + (1/n) \log C_e \qquad (3)$$

$$\textbf{Langmuir isotherms: } (C_e/q) = (1/Q_o b) + (C_e/Q_o) \qquad (4)$$

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 mgL^{-1} or ppm); Q_o and b are Langmuir constants, which are the measures of monolayer adsorption capacity(in mgg^{-1}) and surface energy (in g L^{-1}), respectively. The adsorption data were fitted to these isotherm equations by carrying out correlation analysis and the values of slope (1/n and $1/Q_o$) and intercept (log K and $1/Q_o b$) were obtained. The adsorption isotherm parameter along with the correlation coefficients is presented in table 2. The observed linear relationships are statistically significant at 95% confidence as evidenced by the r-values (very close to unity), which indicate the applicability of these two adsorption isotherms and the monolayer coverage of adsorbate on adsorbent surface [22].

Table 2. Freundlich and Langmuir parameters of adsorption isotherms for the removal of CR by various adsorbents at 30 ±1°C.

Model	Parameters	CAC	EGBC
Freundlich Isotherm	Slope (1/n)	0.412	0.396
	Intercept (log K)	0.675	0.689
	Correlation Coefficient (r)	0.996	0.974
Langmuir Isotherm	Slope ($1/Q_0$)	0.042	0.032
	Intercept ($1/Q_0 b$)	0.285	0.264
	Correlation coefficient (r)	0.989	0.938
	Q_o (mg/g)	35.864	26.789
	b (g/L)	2.998	2.0459
	R_L	0.049	0.034

Further, the essential characteristics of Langmuir isotherm can be described by a separation factor R_L, which is defined by the following equation:

$$R_L = [1 / (1 + b\, C_i)] \quad (5)$$

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

R_L values	**Nature of adsorption process**
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L > 1$	Favourable
$R_L = 0$	Irreversible

In the Present study, the computed values of R_L (Table 2) were found to be in the range 0-1 indicating that the adsorption process was favorable for this low cost adsorbent.

Effect of contact time:

The effect of contact time on the amount of dye adsorbed (q, in mg g^{-1}) was studied at the optimum initial concentration of dye (Table1). The amount of MG adsorbed by these carbons increased and reached a constant value with the increase in contact time [23].The decrease in the removal of dye adsorbed after reaching a constant value (in some cases) may be due to the desorption process. The increase in extent of removal of dye after a particular contact time is less and hence it is fixed as the optimum contact time. The adsorbate species normally forms a surface layer, which is only one molecule thick, that is a monolayer on the surface of the adsorbent.

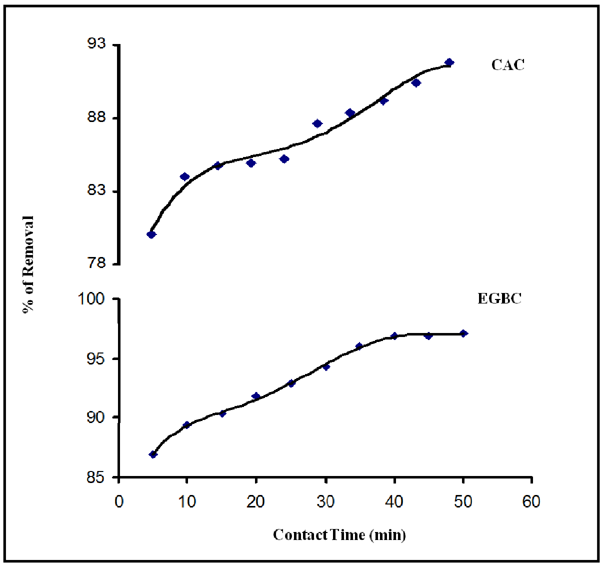

Figure-2 Effect of contact time on the extent removal of MG onto CAC and EGBC.

Kinetics of adsorption:

The kinetics of adsorption of MG by EGBC have been studied by applying various first order kinetic equations proposed by Natarajan and Khalaf as cited by [24], Lagergren as cited by [25] and Bhattacharya and Venkobachar[26].

Natarajan and Khalaf equation	: $\log (C_i / C_t) = (k / 2.303)\, t$	**(6)**
Lagergren's equation	: $\log (q_e - q_t) = \log q_e - [k/2.303]\, t$	**(7)**
Bhattacharya & Venkobachar equation	: $\log[1-U(T)] = -[k/2.303]\, t$	**(8)**

Where C_i and C_t are the concentration of dye (in mg L^{-1} or ppm), at time zero 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 ppm) and k and k_{ad} 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.

Intra-Particle iffusion 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 following equation [27].

$$q_t = k_p t^{½} + C \quad (9)$$

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 *i.e.*, the larger the intercept, the greater is the boundary layer effect [28].

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

Parameters	**Adsorbents**	
	CAC	**EGBC**
Natarajan & Khalaf equation		
Correlation Coefficient (r)	0.991	0.934
10^2K (min^{-1})	4.108	2.815
Lagergren equation		
Correlation Coefficient (r)	0.975	0.947
10^2K (min^{-1})	5.213	47.774
Bhattacharya and Venkobachar equation		
Correlation Coefficient (r)	0.972	0.943
10^2 K (min^{-1})	4.945	53.714
Intra Particle diffusion Model		
K_p	0.943	2.613
Correlation Coefficient (r)	0.967	0.940
Intercept	86.341	52.218
Log (% removal) Vs log (time)		
Slope	0.042	0.205
Intercept	1.888	1.586
Correlation Coefficient (r)	0.965	0.954

Effect of adsorbent dosage:

Figure. 3 represents the effect of dose of the adsorbent EGBC on the extent removal of MG and the relevant data are given in table 1. The relative extent of removal of MG (in terms of q) is found and $4gL^{-1}$ for EGBC, which fixed as the optimum dose of adsorbent. The amount of dye adsorbed was observed to vary exponentially in accordance with a fractional power term of the dose of adsorbent $(dose)^{-n}$ where n = fraction. The plots of log (dose) vs log (% removal) are found to be linear (r ≈ 1.0). This suggests that the adsorbed species / solute may either block the access to the internal pores or cause particles to aggregate and thereby resulting in decrease in the availability of active sites for adsorption [29].

Effect of initial pH:

The effect of initial pH of the dye solution on the amount of dye adsorbed on EGBC 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. This result is in harmony with the literature reports [30], the final pH of the dye (MG) solution after adsorption was found be increases, due to adsorption of the basic form of dye molecule.

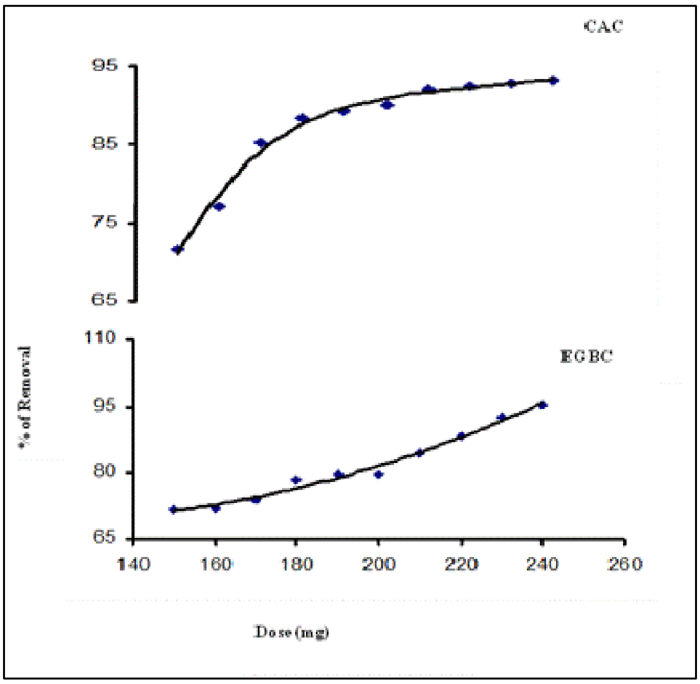

Figure -3 Effect of dose for the removal of MG onto CAC and EGBC.

Table 4 - Effect of initial pH for removal of MG by CAC and EGBC at 30 ±1°C

S.No	Initial pH	Percentage Removal (%)		Amount Adsorbed (in mg/L)	
		CAC	EGBC	CAC	EGBC
1	2.0	65.89	68.00	24.55	22.90
2	3.0	73.89	73.00	26.35	25.95
3	4.0	75.40	76.33	28.23	28.95
4	5.0	78.25	80.66	31.25	32.02
5	6.0	83.58	84.66	33.56	34.71
6	7.0	87.76	86.00	36.89	36.97
7	8.0	89.56	89.66	38.56	37.25
8	9.0	92.26	92.00	41.23	39.56
9	10	94..36	93.83	42.89	41.98
10	11	97.28	96.00	46..35	43.24

Effect of particle size:
The effect of particle size of the adsorbent on the extent of removal of dyes on EGBC was studied under constant optimum experimental conditions by varying the particle size.The effect of particle size variation of an adsorbent on the extent of removal of dye, indicates that the rate of dye uptake increase with the decrease in particle size. This is due to the increase in the availability of surface area of the adsorbent with the decrease in particle size [32].

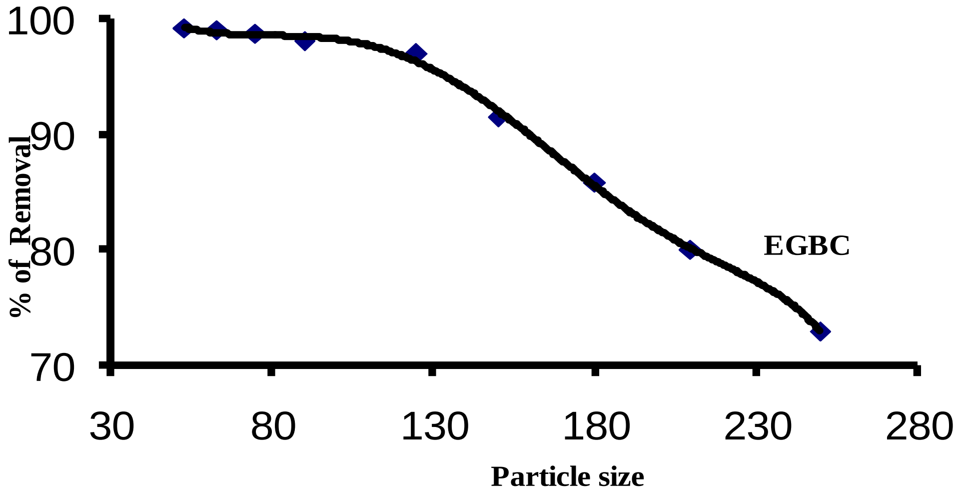

Figure-4 Effect of particle size for the removal of MG on EGBC

CONCLUSION

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 EGBC and increases in contact time, dose of adsorbent and initial pH of the dye solution. Adsorption data obeyed Frendlich and Langmuir adsorption isotherms and first order kinetic equations. The intra-particle diffusion is one of the rate determining steps, and prepared EGBC could be employed as adsorbent for the removal of dye / color in general and Malachite Green (MG) in particular.

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