

Adsorption of Malachite Green Using a Low-Cost Activated Carbon Prepared From *Cassia fistula*

N. Renugadevi, M. Sharfunisha and P. Lalitha

Avinashilingam Deemed University for Women, Department of Chemistry, Coimbatore-641 043

In the present study the efficiency of the carbon adsorbent prepared from the *Cassia fistula* seeds was tested for the removal of malachite green dye from aqueous solution. The parameters, such as pH, adsorbent dosage and initial dye concentration were systematically evaluated. It is an N- methylated diaminotriphenyl methane dye widely used for colouring purpose and highly cytotoxic to mammalian cells. The percentage removal of malachite green increased with concentration of the dye solution. Nearly 40% adsorption was noted at pH 10 in 180 min of contact time at initial concentration of 400 mg/L with 300 mg of the low-cost adsorbent. Removal of malachite green increased from 24.05 to 28.23% with increasing adsorbent dosage from 300 to 600 mg in 180 min of agitation time, using 100 mL of dye solution of initial concentration of 400 mg/L. Langmuir adsorption isotherm plots and Freundlich adsorption isotherm plots were linear showing the applicability of the isotherms for malachite green adsorption.

KEYWORD

Cassia fistula, Langmuir, Freundlich, Adsorption.

INTRODUCTION

Industrial effluents from dyeing industries are one of the major causes of environmental pollution because effluents discharged from dyeing industries are highly coloured with a large amount of suspended organic solids. Untreated disposal of this coloured water into the receiving water body causes damage to aquatic life and human beings by their mutagenic and carcinogenic effect. The discharge of such effluents is worrying for both toxicological and environmental reasons (Baskaran *et al.*, 2010). Adsorption is usually described through isotherms, that is the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. Adsorption is operative in most natural, physical, biological and chemical systems and is widely used in industrial applications, such as activated charcoal, synthetic resins and water purification

(Godbole *et al.*, 2006). Malachite green is an N- methylated diaminotriphenyl methane dye widely used for colouring purpose. It is highly cytotoxic to mammalian cells and also acts as a liver tumor enhancing agent (Baskaran *et al.*, 2010). A successful adsorption process not only depends on dye adsorption performance of the adsorbent, but also on the constant supply of the materials for the process. So it is preferable to use low-cost adsorbents. Such low-cost adsorbents have given satisfactory performance at the laboratory scale for the treatment of coloured effluents. To improve the efficiency of adsorption process it is necessary to develop cheap and easily available adsorbents with high adsorption capacities (Rajeshkannan *et al.*, 2010). In the present study the efficiency of the carbon adsorbent prepared from the *Cassia fistula* seeds was tested for the removal of malachite green dye from aqueous solution. The parameters, such as pH, adsorbent dosage and initial dye concentration were systematically evaluated.

MATERIAL AND METHOD

	mg/L	mg/L	mg/L	mg/L
10	10.17	9.23	8.33	7.59
20	11.87	10.77	9.72	8.86
30	13.55	12.31	11.11	10.12
40	15.25	13.84	12.50	11.39
50	16.95	15.38	13.89	12.65
60	18.65	16.92	15.28	13.92
90	20.33	20.00	18.05	16.45
120	23.72	21.54	20.83	18.98
150	25.42	24.61	22.22	21.52
180	28.81	27.69	25.00	24.05

Table 2. Adsorption of malachite green with variation of pH

Conditions :

Adsorbent dosage : 300mg

Temperature : 37°C

Concentration of dye solution : 400mg/L

Contact time : 10 to 180 min

Time, min	% Adsorption of malachite green			
	pH 7.0	pH 8.0	pH 9.0	pH 10.0
10	9.09	10.41	13.26	17.02
20	10.22	11.45	15.30	19.14
30	11.36	12.50	17.34	21.27
40	12.50	13.54	19.38	23.40
50	13.63	15.62	21.42	25.53
60	14.77	17.70	24.48	27.65
90	18.81	20.00	27.55	30.85

30	10.12	10.59	11.76	14.12
40	11.39	11.76	12.92	15.29
50	12.65	12.94	14.12	16.47
60	13.92	14.12	15.29	17.94
90	16.45	17.94	18.82	20.00
120	18.98	20.00	21.17	22.35
150	21.52	22.35	23.53	24.70
180	24.05	25.88	27.06	28.23

cost carbon adsorbent used in this study for the removal of malachite green was prepared from the seeds of *Cassia fistula*.

Preparation of the adsorbent

Seeds of *Cassia fistula* were collected from Avinashilingam Deemed University Campus, Coimbatore. The collected pods were cut into small pieces, dried in sunlight for 5 day and further dried in a hot air oven at 60°C for 24 hr. The completely dried material was powdered well. The powdered raw material was chemically activated by treating with concentrated sulphuric acid with constant stirring and kept for 24 hr. The carbonized material was washed well with plenty of water several times to remove excess acid and dried at 105-110°C in a hot air oven.

Reagent

The dye solution was prepared by dissolv-

Table 4. Interpretation of results of adsorption of malachite green in terms of Langmuir adsorption isotherm for variation of initial concentration of dye solution

Time, min	Initial conc. of dye, mg/L	$1/C_e$	m/x	Separation factor R_L	Intercept k_1/k_1^1	Slope $1/k_1^1$
10	100	0.1113	0.2949	0.0227	0.03506	2.33135
	200	0.0551	0.1624	0.0115		
	300	0.0363	0.1199	0.0077		
	400	0.02705	0.0987	0.0057		
20	100	0.1134	0.2527	0.0191	0.03047	1.95714
	200	0.0560	0.1392	0.0096		
	300	0.0369	0.1028	0.0064		
	400	0.0274	0.0846	0.0048		
30	100	0.1156	0.2214	0.0165	0.02678	1.68128
	200	0.0570	0.1218	0.0083		
	300	0.0375	0.0899	0.0055		
	400	0.0278	0.0740	0.0041		
40	100	0.1180	0.1967	0.0143	0.02433	1.4590
	200	0.0580	0.1083	0.0072		
	300	0.0380	0.0799	0.0048		
	400	0.0282	0.0658	0.0036		
50	100	0.1204	0.1769	0.0126	0.02217	1.28367
	200	0.0590	0.0974	0.0063		
	300	0.0387	0.0719	0.0042		
	400	0.0286	0.0592	0.0031		
60	100	0.1229	0.1608	0.0112	0.02050	1.1404
	200	0.0601	0.0886	0.0056		
	300	0.0393	0.0654	0.0037		
	400	0.0290	0.0538	0.0028		
90	100	0.1255	0.1475	0.0106	0.01125	1.07609
	200	0.0625	0.0749	0.0053		
	300	0.0406	0.0553	0.0035		
	400	0.0299	0.0455	0.0026		
120	100	0.1311	0.1264	0.0086	0.01247	0.87185
	200	0.0637	0.0696	0.0043		
	300	0.0421	0.0479	0.0028		
	400	0.0308	0.0394	0.0021		
150	100	0.1341	0.1180	0.0080	0.009009	0.80931
	200	0.0663	0.0609	0.0040		
	300	0.0428	0.0449	0.0026		
	400	0.0318	0.0348	0.0020		
180	100	0.1404	0.1041	0.0067	0.008964	0.67483
	200	0.0691	0.0541	0.0033		
	300	0.0444	0.0400	0.0022		
	400	0.0329	0.0312	0.0016		

for spectro colourimetric work. Genuine equipment manufacturer's mechanical hori-

zontal bench shaker was used for the shaking of solution containing adsorbent and ad-

	400	1.5617	1.0726
30	100	0.9367	0.6548
	200	1.2439	0.9143
	300	1.4259	1.0462
	400	1.5556	1.1307
40	100	0.9280	0.7061
	200	1.2362	0.9653
	300	1.4191	1.0974
	400	1.5495	1.1817
50	100	0.9193	0.7522
	200	1.2284	1.0114
	300	1.4121	1.1432
	400	1.5432	1.2276
60	100	0.9103	0.7937
	200	1.2205	1.0525
	300	1.4051	1.1844
	400	1.5369	1.2692
90	100	0.9012	0.8321
	200	1.2040	1.1255
	300	1.3906	1.2572
	400	1.5106	1.3419
120	100	0.8823	0.8982
	200	1.1956	1.1573
	300	1.3756	1.3196
	400	1.5106	1.4045
150	100	0.8725	0.9281

-0.0616	0.7734	1.2928
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-0.00027	0.7698	1.2989
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0.0557	0.7665	1.3046
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0.1070	0.7632	1.3102
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0.00811	0.9160	1.0916
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0.1785	0.8189	1.2210
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0.2022	0.8423	1.1871
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sorbate.

Effect of variation of initial concentration of the dye on the adsorption

The dye solution of different concentrations containing 10, 20, 30 and 40 mg of dye in 100 mL was added with 300 mg of the adsorbent taken in pyrex bottles and shaken in a mechanical horizontal bench shaker for various time intervals (10, 20, 30, 40, 50, 60, 90, 120, 150, and 180 min) at room temperature. The solutions were filtered and the dye concentrations of the filtrates were estimated colourimetrically at 620 nm.

Effect of variation of pH on the adsorption of dye

The optimum pH for the maximum dye adsorption was found by varying the pH from 7.0 to 10.0. The pH of the prepared original dye solution was 2.87. Therefore, pH of the solution for this pH variation study was adjusted using dilute sodium hydroxide. 100 mL of the dye solution containing 400 mg of the dye were contacted with 300 mg of the adsorbent and batch mode experiments conducted by varying the pH from 7.0 to 10.0. These solutions were shaken using mechanical horizontal bench shaker for various time intervals (10, 20, 30, 40, 50, 60, 90, 120, 150 and 180 min). The solutions were filtered and the filtrates obtained analyzed colourimetrically to find the amount of dye adsorbed.

Effect of variation of adsorbent dosage on the adsorption of dye

100 mL of the dye solution containing 400 mg of the dye were taken in pyrex bottles and batch adsorption studies conducted by varying the adsorbent dosage (300, 400, 500, 600 mg). The pyrex bottles containing adsorbent and adsorbate were shaken using mechanical horizontal bench shaker at room temperature for various time intervals (10, 20, 30, 40, 50, 60, 90, 120, 150 and 180 min). Then solutions were filtered and the filtrates were analyzed colourimetrically to find out the amount of dye adsorbed.

RESULT AND DISCUSSION

The results were used to evaluate the optimum conditions for the removal of the dye, malachite green and to examine the efficiency of the low-cost adsorbent prepared in this study for the treatment of aqueous solution containing malachite green. The parameters which influence the extent of adsorption, such as concentration of the adsorbate, contact time, pH and adsorbent dosage were investigated.

Effect of variation of initial concentration of malachite green solution on adsorption of malachite green from aqueous solution

The percentage removal of malachite green with the variation in initial concentration of malachite green solution is given in table 1. An increase in percentage removal (24.05 to 28.81%) of malachite green noticed when the initial concentration of adsorbate was varied from 400 to 100 mg/L. This may be probably due to the fact that for a fixed adsorbent dose, the total available adsorption sites are limited there by adsorbing almost the same amount of malachite green corresponding to an increased initial concentration of the adsorbate.

Effect of pH variation on adsorption of malachite green

In order to optimize the pH for maximum malachite green removal experiments were conducted with 100 mL of aqueous solution of the dye containing 400 mg/L of malachite green solution with 300 mg adsorbent by varying the pH from 7 to 10 at various contact time (10, 20, 30, 40, 50, 60, 90, 120, 150 and 180 min) and the results are depicted in table 2. The percentage adsorption of dye increased from 28.40 to 40.42%, when the pH is varied from 7 to 10. The results indicated a maximum adsorption of dye (~40.42%) at pH 10.

Effect of adsorbent dosage on adsorption of malachite green

The effect of variation of adsorbent dosage was determined by varying the adsorbent dosage from 300 to 600 mg. The results have been tabulated in table 3. It is evident

tion that points of valency exists on the surface of the adsorbent and that each of these site is capable of adsorbing one molecule. The Langmuir model assumes that uptake of adsorbate occurs on a homogeneous surface by monolayer adsorption (Sharma *et al.*, 2009). Thus the adsorbed layer will be one molecule thick. Further, it is assumed that all the adsorption sites have equal affinities for the adsorbent and that the presence of adsorbed molecules at one site will not affect the adsorption of a molecule at an adjacent site. The Langmuir adsorption isotherm is commonly given by :

$$x/m = (k_1^1 C_e / 1 + k_1^1 C_e)$$

where, x is amount of malachite green adsorbed (mg/L), m is weight of adsorbent (mg), C_e is concentration of malachite green at equilibrium and k_1^1 and k_1 is Langmuir constants (adsorption capacity and energy of adsorption).

on rearranging,
$$\frac{1}{x/m} = \frac{1}{k_1^1/k_1} + \frac{1}{k_1^1/C_e}$$

The plot of $1/(x/m)$ vs $1/C_e$ is linear with slope equal to $1/k_1^1$ and intercept $[1/(k_1^1/k_1)]$. The slope, intercept and separation factor values are calculated and given in the table 4. The linear plots ($r > 0.8$) of $1/C_e$ vs

the n_L values obtained in this study was below one (Table 4) and this shows the feasibility of the adsorption process at all initial concentrations of malachite green used in this study.

Freundlich adsorption isotherm : Attempts were made to fit the data into Freundlich adsorption isotherm (Table 5). The equilibrium data at room temperature has been processed in accordance with Freundlich adsorption isotherm given by the equation :

$$x/m = K_f C_e^{1/n}$$

$$\log x/m = \log K_f + 1/n \log C_e$$

where x/m is the amount of malachite green adsorbed on unit weight of adsorbent at equilibrium (Jambulingam *et al.*, 2005). The linear form of Freundlich adsorption isotherm at room temperature is plotted between $\log x/m$ vs C_e for different initial concentrations of the aqueous solutions of malachite green solution with the 300 mg of the adsorbent. K_f and $1/n$ values are evaluated from the slope and intercept, respectively. The Freundlich parameters K_f and $1/n$ are indicators of adsorption capacity and adsorption intensity, respectively (Table 5).

CONCLUSION

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tration dependent. Removal of malachite green dye increases with increase in pH. Nearly 40% adsorption was noted at pH 10 in 180 min of contact time at initial concentration of 400 mg/L with 300 mg of the low-cost adsorbent. Removal of malachite green increased from 24.05 to 28.23% with increasing adsorbent dosage from 300 to 600 mg in 180 min of agitation time, using 100 mL of dye solution of initial concentration of 400 mg/L. Langmuir adsorption isotherm plots and Freundlich adsorption isotherm plots were linear showing the applicability of the isotherms for malachite green adsorption. The low-cost activated carbon derived from the seed of *Cassia fistula* can be used as an efficient adsorbent for the removal of a basic dye, malachite green from aqueous solution.

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REFERENCE

Baskaran, P.K., B.R. Venkataraman and S. Arivoli. 2010. Adsorption of malachite green dye by acid activated carbon-Kinetic, thermodynamic and equilibrium studies

- (zea mays). *E-J. Chemistry*, 8(1) : 9-18.
- Godbole, P.T. and A.D., Sawant. 2006. Removal of malachite green from aqueous solution using immobilized *Saccharomyces cerevisiae*. *J. Sci. Ind. Res.*, 65:440-442.
- Jambulingam, M., et al. 2005. Adsorption of Cr(VI) from aqueous solution using a low-cost activated carbon. *Indian J. Env. Prot.*, 25(5) : 458-463.
- Rajeshkannan, R., M. Rajasimman and N. Rajamohan. 2010. Decolourisation of malachite green using tamarind seed : Optimization, isotherm and kinetic studies. *Chem. Ind. Chem. Eng. Quarterly*, 17 (1): 67-79.
- Sharma, Y., C. Singh and B. Uma. 2009. Fast removal of malachite green by adsorption of rice husk activated carbon. *The Open Env. Poll. Toxicology J.*, 1:74-78.

AUTHOR

- 1*. Dr.N.Renugadevi, Associate Professor, Department of Chemistry, Avinashilingam Deemed University for Women, Coimbatore-641 043.
2. Ms. M. Sharfunisha, M.Sc Student, Department of Chemistry, Avinashilingam Deemed University for Women, Coimbatore-641 043.
3. Dr. P. Lalitha, Assistant Professor, Department of Chemistry, Avinashilingam Deemed University for Women, Coimbatore-641 043.