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Removal of Malachite Green from Aqueous Solution using *Hydrilla verticillata* - Optimization, Equilibrium and Kinetic Studies

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***Abstract*—**In this study, the sorption of Malachite green (MG) on Hydrilla verticillata biomass, a submerged aquatic plant, was investigated in a batch system. The effects of operating parameters such as temperature, adsorbent dosage, contact time, adsorbent size, and agitation speed on the sorption of Malachite green were analyzed using response surface methodology (RSM). The proposed quadratic model for central composite design (CCD) fitted very well to the experimental data that it could be used to navigate the design space according to ANOVA results. The optimum sorption conditions were determined as temperature - 43.5°C, adsorbent dosage - 0.26g, contact time - 200min, adsorbent size - 0.205mm (65mesh), and agitation speed - 230rpm. The Langmuir and Freundlich isotherm models were applied to the equilibrium data. The maximum monolayer coverage capacity of Hydrilla verticillata biomass for MG was found to be 91.97 mg/g at an initial pH 8.0 indicating that the optimum sorption initial pH. The external and intra particle diffusion models were also applied to sorption data of Hydrilla verticillata biomass with MG, and it was found that both the external diffusion as well as intra particle diffusion contributes to the actual sorption process. The pseudo-second order kinetic model described the MG sorption process with a good fitting.

***Keywords*—**Response surface methodology, *Hydrilla verticillata*, malachite green, adsorption, central composite design

I. INTRODUCTION

THE discharge of highly colored 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 are 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 [1]. Wastewaters from dyeing industries are 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 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 [2], However the adsorption capacities of the above adsorbents are not very high. In order to improve the efficiency of the adsorption processes, it is necessary to develop cheap and easily available adsorbents with high adsorption capacities. In a world of rapid assimilation of natural resources, any attempt at the utilization of agricultural waste augments the raw material stock and also provides additional employments and income to marginal farmers and landless agricultural labourers, especially in developing countries like India. *Hydrilla verticillata*, a submerged aquatic plant found widely in India, is listed as one of the most productive plants on earth and is considered as one of the world's worst aquatic plants. It forms dense mats that interfere with navigation, recreation, irrigation, and power generation.

This study is focused to utilize the *Hydrilla verticillata* as a potential adsorbent to remove malachite green from the aqueous solutions. Malachite green is widely used for coloring purpose, among all the other dyes of its category. Malachite green has wider applications that include coloring paper, coloring leather products, dyeing cotton, wool, silk, and jute and also used in distilleries [3,4].

The application of statistical experimental design techniques in adsorption process development can result in improved product yields, reduced process variability, closer confirmation of the output response to nominal and target requirements and reduced development time and overall costs. This methodology is widely used in chemical engineering, notably to optimize the adsorption process [5,6,7]. In this study, the combined effect of pH, adsorbent dose, temperature, initial dye concentration and

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contact time on malachite green dye removal from aqueous medium by *Hydrilla verticillata* has been investigated using CCD in RSM.

II. MATERIALS AND METHODS

A. Preparation of Sorbent

The *Hydrilla verticillata* used in this study were obtained from a pond near by the Department of Chemical Engineering, Annamalai University, Tamil Nadu, India. The collected biomaterial was extensively washed with tap water to remove soil and dust and sliced into pieces. The sliced material was dried by exposure to the sunlight for 3 days and subsequently at 80ºC for 3 h in a hot air convection oven. The dried material was milled in to a powder using a domestic mixer and was allowed to pass through a different mesh opening size sieve.

B. Preparation of aqueous dye solutions

Malachite green was obtained from CDH chemicals, New Delhi, India and was further used without any purification. All other reagents were of analytical reagent grade and were obtained from Qualigens Fine Chemicals, Mumbai, India. The structure of the malachite green used in the present study was shown in Fig. 1. The detail of the malachite green is given in Table 1. A calculated amount of the dye was dissolved separately in 1 L of deionized water to prepare stock solutions, which were kept in dark colored glass bottles. For batch study, an aqueous solution of this dye was prepared from stock solutions in deionized water. The concentration in the test solution was determined spectrophotometrically using a UV–Double beam spectrophotometer, (HITACHI 2101) at a wavelength corresponding to the maximum absorbence (619 nm). The pH of the solution was adjusted using 0.1 mol/L HCl or NaOH using a pH (Orion 420) meter. All the used chemicals were of analytical grade.

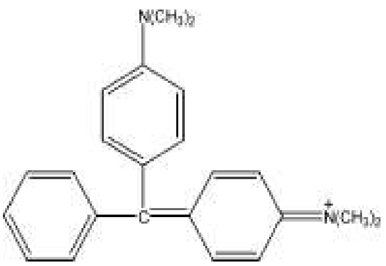


Fig. 1 Chemical structure of malachite green

C. Experimental design by RSM

RSM is an empirical statistical technique employed for multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously. A full factorial design, which includes all possible factor combinations in each of the factors, is a powerful tool for understanding complex processes for describing factor interactions in multifactor systems. In order to describe the effects of temperature, adsorbent dosage, contact time, particle size and agitation speed on the % removal of malachite green dye, batch experiments were conducted based on the central composite design. The coded values of the process parameters were determined by the following equation

$$x_i = \frac{X_i - X_o}{\Delta x}, \tag{1}$$

where x_i – coded value of the ith variable, X_i – uncoded value of the ith test variable and X_0 – uncoded value of the ith test variable at center point.

The range and levels of individual variables are given in Table 1. The experimental design is given in Table 2, along with experimental data and predicted responses. The regression analysis was performed to estimate the response function as a second order polynomial

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1,i<j}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \tag{2}$$

Where Y is the predicted response, β_i, β_j, β_{ij} are coefficients estimated from regression. They represent the linear, quadratic and cross products of x_1, x_2, x_3 on response.

TABLE I
LEVELS OF DIFFERENT PROCESS VARIABLES IN CODED AND UN-CODED FORM FOR ADSORPTION OF MALACHITE GREEN

Variable	**Code**	**Levels**				
		-2.38	**-1**	**0**	**+1**	**+2.38**
Temperature, ºC	A	35	40	45	50	55
Sorbent dosage, g	B	0.1	0.2	0.3	0.4	0.5
Contact time, min	C	150	200	250	300	350
Particle size, mm	D	0.35	0.246	0.17	0.124	0.074
Stirring Speed, rpm	E	100	150	200	250	300

A statistical program package Design Expert 7.1.5, was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equations were validated by the statistical tests called the ANOVA analysis. The significance of each term in the equation is to estimate the goodness of fit in each case. Response surfaces were drawn to determine the individual and interactive effects of the test variable on the % removal of malachite green dye. The optimal values of the test variables were first obtained in coded units and then converted to the uncoded units.

D. Experimental procedure

The adsorption of Malachite green from aqueous solution on to *Hydrilla verticillata biomass* was performed under shaking conditions in an orbital shaker (REMI-12, India). The experiments were performed according to the central composite design. To each 100 mL solution of Malachite green, a desired quantity of the *Hydrilla verticillata biomass* was added in 250mL Erlenmeyer flasks. The mixture was agitated in an incubated orbital shaker at the desired temperature and desired speed for predetermined time intervals. The supernatant was agitated by centrifugation at 4000 rpm for 10 min. The residual concentration in the supernatant was determined. The dye concentration in raw and treated sample was determined by UV-Vis (Elico, SL 164, Hydarabad, India) Spectrophotometer. The analyses were carried out at a wavelength of 619nm in a UV-Vis Spectrophotometer. A calibration plot for malachite green was drawn between % absorbance and standard dye solutions of various strengths. From the noted absorbance value the initial concentration, the concentration of the treated dye sample was determined. The response, i.e., removal efficiency of Malachite green was calculated as

$$Y(\%) = \frac{(C_o - C_i)}{C_o} \times 100 \cdot \qquad (3)$$

Where Co, Ci are the initial and final concentration of the dye solution. All experiments were carried out in triplicate and the mean values were reported. The maximum deviation was found to be ±3%

The process variables, temperature, adsorbent dosage, contact time, particle size and agitation speed were optimized and at these optimized conditions, the effect of pH and initial dye concentration were studied. The amount of equilibrium adsorption, q_e (mg/g), was calculated by:

$$q_e = \frac{V(C_o - C_e)}{M} \qquad (4)$$

where C_0 and C_e (mg/l) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. *V* (L) is the volume of the solution and *M* (g) is the mass of dry sorbent used.

III. Results and discussion

A. *Experimental design and fitting of quadratic model*

To examine the combined effect of five different process parameters (independent variables), on % color removal of malachite green, 50 experiments were performed. Eq. (5) represents the mathematical model relating the % color removal with the independent process variables and the second order polynomial coefficient for each term of the equation determined through multiple regression analysis using the Design Expert 7.1.5. The experimental and predicted values of removal of malachite green were given in Table 2.

$$\%\text{decolorization} = 82.33 - 1.75\,A + 0.144\,B - 4.48\,C - 1.44\,D + 6.23E + 5.64\,AB + 2.75\,AC - 2.53\,AD + 1.25\,AE + 3.25\,BC - 1.32\,BD + 4.32\,BE + 3.31CD - 1.32\,CE + 0.028\,DE - 8.07\,A^2 - 3.56\,B^2 - 4.3\,C^2 - 3.2\,D^2 - 7.3\,E^2 \qquad (5)$$

The results were analyzed by using ANOVA i.e. and shown in Table 3. The ANOVA of the quadratic regression model indicates the model to be significant. The Model F-value of 9.95 implies that the model is significant. The smaller the magnitude of the P, the more significant is the corresponding coefficient. Values of P less than 0.05 indicate the model term is significant. From the P values it was found that, among the test variables used in the study, C, E, AB, BC, BE, CD, A^2, B^2, C^2, D^2, E^2 are significant model

The predicted R^2 of 0.7671 is in reasonable agreement with the adjusted R^2 of 0.8332. The fit of the model was also expressed by the coefficient of regression R^2, which was found to be 0.9188, indicating that 91.88% of the variability in the response, could be explained by the model. This implies that the prediction of experimental data is quite satisfactory.

TABLE II
EXPERIMENTAL CONDITIONS AND OBSERVED RESPONSE VALUES OF CCD

Run	A	B	C	D	E	% Decolurisation	
						Experimental	Theoretical
1	-1	-1	1	-1	1	48.3	48.63
2	-1	1	1.	1	-1	50.1	40.45
3	-1	1	-1.	1.	1	65.4	65.46
4	0	0	0	0.	0	82.5	82.33
5	1	-1	-1	1	1	49.0	49.11
6	1	1	1.	1.	1	60.0	67.37
7	0.	0.	0.	-2.38	0.	68.0	67.19
8	1.	1	1	-1	1.	67.0	71.32
9	1	1	-1	-1.	1	69.0	77.34
10	0	0	0.	0.	0.	82.5	82.33
11	1.	1.	-1	1.	1	60.0	60.16
12	-1	1.	-1	1	-1	30.0	39.29
13	0	0	0.	0	0	82.5	82.33
14	1	1.	-1.	-1	-1	64.0	56.31
15	2.38	0	0	0	0	40.8	32.48
16	0	0.	0	0	0	82.5	82.33
17	1	1	-1	1	-1	38.0	39.01
18	1	-1	1	-1	1	50.2	41.92
2	0	2.38	0.	0.	0	61.2	62.49
21	1	1.	1.	-1.	-1	59.0	55.23
22	-	-1.	-1.	-1	1	69.0	78.71
23	1	-1	1.	1	1	35.0	43.29
24	1	-1	-1	-1.	-1	46.9	57.26
25	-1	1	1.	-1	-1	35.0	43.29
26	-1.	1	1.	1	1	68.0	61.66
27	-1.	-1	-1.	1.	-1	79.0	69.97
28	-1	-1	-1.	-1.	-1	79.0	68.12
29	-1	-1	1	1	-1.	47.8	56.22
30	1	-1	1	1	-1	55.3	44.39
31	-1	-1	1.	-1	-1.	50.0	44.83
32	0	0	0.	0	-2.38	18.2	25.66
33	1	-1	1.	-1	-1.	37.0	43.12
34	0	0	0	0	0.	82.5	82.33
35	-1	1	-1	-1.	-1	44.0	46.46
36	0	0	0	0.	0.	82.5	82.33
37	0	-2.38	0.	0.	0	65.6	61.80
38	1	-1	-1	1	-1.	38.0	45.23
39	-2.38	0	0	0	0	35.0	45.80
40	0	0	0	0.	2.38	65.3	55.47
41	-1	-1	1	1.	1	62.0	60.13
42	-1	1	1	-1.	1	55.0	55.47
43	0	0	0.	0	0	82.5	82.33
44	0	0	-2.38	0.	0	78.0	68.65
45	-1	-1	-1	1.	1	70.3	76.93
46	-1	1	-1	-1	1	76.0	72.51
47	0	0	0.	2.38	0	62.0	60.29
48	1	-1	-1	-1	1	59.0	60.98
49	1.	1	1	1	-1	52.0	51.16
50	0	0	2.38	0	0	40.5	47.34

B. *Response surface estimation for maximum removal of Malachite green*

As discussed in previous section, response surface methodology was used with five process variables to evaluate their effect on the adsorption process. To investigate the interactive effect of two factors on the removal of dye, response surface methodology was used and three-dimensional plot was drawn. The inferences so obtained are discussed below.

Response surface plots as a function of two factors at a time, maintaining all other factors at fixed levels are more helpful in understanding both the main and the interaction effects of these two factors. The response surface curves were plotted to understand the interaction of the variables and to determine the optimum level of each variable for maximum response. The response surface curves for %color removal were shown in Figures 2-11. The nature of the response surface curves shows the interaction between the variables. The elliptical shape of the curve indicates good interaction of the two variables and circular shape indicates no interaction between the variables. From figures it was observed that the elliptical nature of the contour in graphs depicted the mutual interactions of all the variables. There was a relative significant interaction between every two variables, and there was a maximum predicted yield as indicated by the surface confined in the smallest ellipse in the contour diagrams.

TABLE III
ANALYSIS OF VARIANCE (ANOVA) FOR RESPONSE SURFACE QUADRATIC MODEL

Source	Sum of square	DF	Mean square	F	P>F
Model	12126.63	20	606.33	9.95	< 0.0001
A	132.32	1	132.33	2.17	0.1513
B	0.90	1	0.90	0.015	0.9042
C	869.73	1	869.73	14.28	0.0007
D	90.97	1	90.97	1.49	0.2315
E	1684.61	1	1684.61	27.65	<0.0001
A*A	3618.16	1	3618.2	59.39	<0.0001
B*B	704.79	1	704.79	11.57	0.0020
C*C	1025.07	1	1025.07	16.83	0.0003
D*D	597.29	1	597.29	9.80	0.0040
E*E	3033.56	1	3033.56	49.80	<0.0001
A*B	1018.13	1	1018.13	16.71	0.0003
A*C	242.55	1	242.55	3.98	0.0555
A*D	205.54	1	205.54	3.37	0.0765
A*E	50.25	1	50.25	0.82	0.3712
B*C	339.25	1	339.95	5.58	0.0251
B*D	56.45	1	56.45	0.93	0.3437
B*E	599.45	1	599.45	9.84	0.0039
C*D	350.46	1	350.46	5.75	0.0231
C*E	48.76	1	48.76	0.80	0.3783
D*E	.025	1	0.025	0.000415	0.9839
Residual	1766.59	29	60.92		
Lack of	1766.59	22	80.30		
fit	0.000	7	0.000		
Pure	13893.22	49			
Error					
Cor Total					

Std. Dev. 7.80 ; R^2 0.9188; mean 59.26; adjusted R^2 0.8332; C.V. %13.17; predicted R^2 .7661

The magnitude of P and F values in Table 3 gives the maximum positive contribution of temperature, adsorbent dosage, contact time, adsorbent size, and agitation speed on the % color removal. The quadratic terms of temperature, adsorbent dose, contact time, adsorbent size and agitation speed have negative effect on % color removal. Further, the interactions of ‘, temperature and adsorbent dosage’ ‘adsorbent dosage and contact time’, ‘temperature and agitation speed’, ‘sorbent dosage and agitation speed’, particle size and agitation speed have positive effect, whereas the interactions of ‘temperature and contact time’ and ‘temperature and adsorbent size’, sorbent dosage and contact time’ , ‘adsorbent dosage and particle size’ and ‘contact time and particle size’ have negative effect on % color removal.

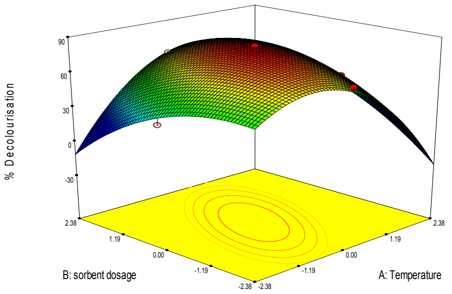


Fig. 2. Response surface plot of the combined effects of temperature and sorbent dosage on the % color removal of malachite green by *Hydrilla verticillata*

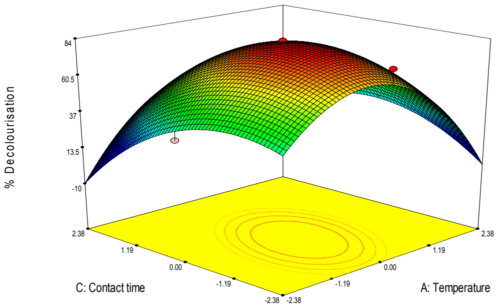


Fig. 3. Response surface plot of the combined effects of temperature and contact time on the % color removal of malachite green by *Hydrilla verticillata*

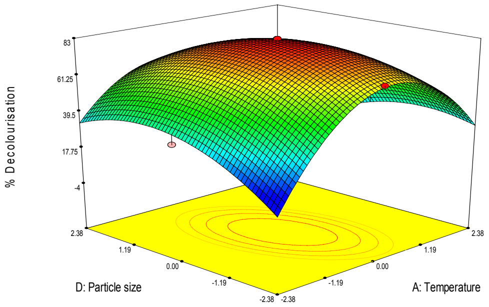


Fig. 4. Response surface plot of the combined effects of temperature and particle size on the % color removal of malachite green by Hydrilla verticillata

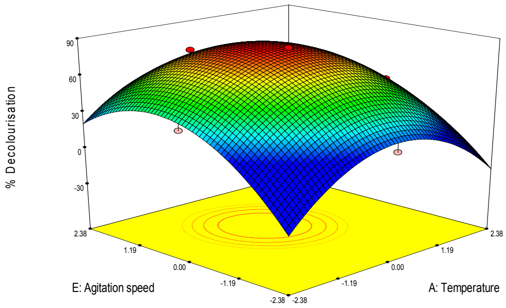


Fig. 5. Response surface plot of the combined effects of temperature and agitation speed on the % color removal of malachite green by *Hydrilla verticillata*

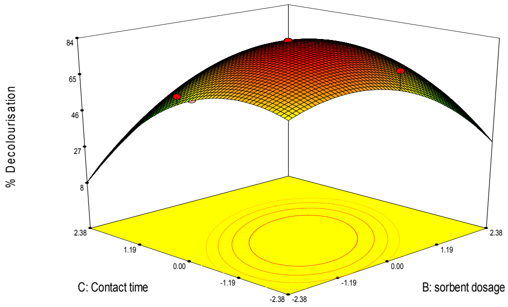


Fig. 6. Response surface plot of the combined effects of contact time and sorbent dosage on the % color removal of malachite green by *Hydrilla verticillata*

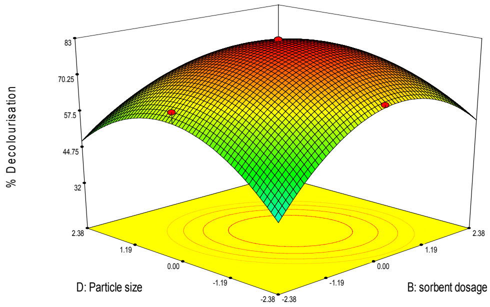


Fig. 7. Response surface plot of the combined effects of particle size and sorbent dosage on the % color removal of malachite green by *Hydrilla verticillata*

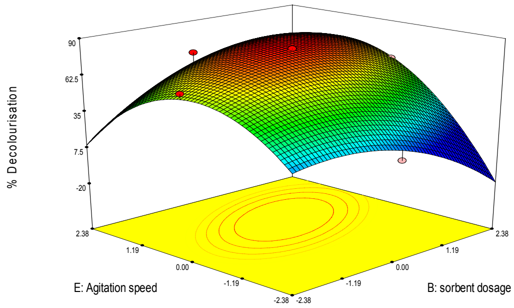


Fig. 8. Response surface plot of the combined effects of agitation speed and sorbent dosage on the % color removal of malachite green by *Hydrilla verticillata*

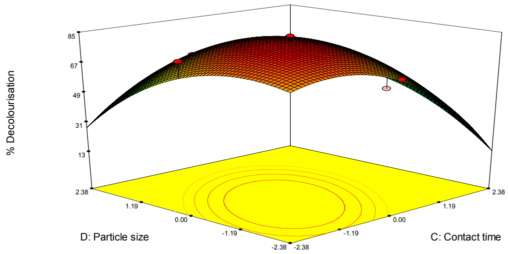


Fig. 9. Response surface plot of the combined effects of contact time and particle size on the % color removal of malachite green by *Hydrilla verticillata*

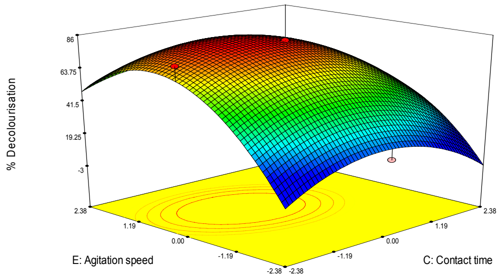


Fig. 10. Response surface plot of the combined effects of contact time and agitation speed on the % color removal of malachite green by *Hydrilla verticillata*

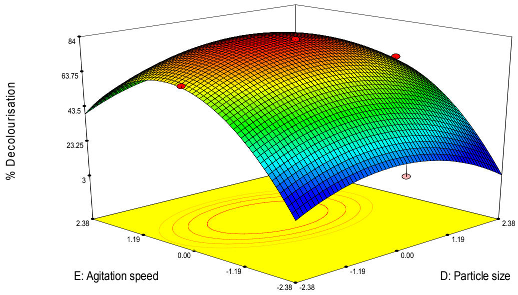


Fig. 11. Response surface plot of the combined effects of particle size and agitation speed on the % color removal of malachite green by *Hydrilla verticillata*

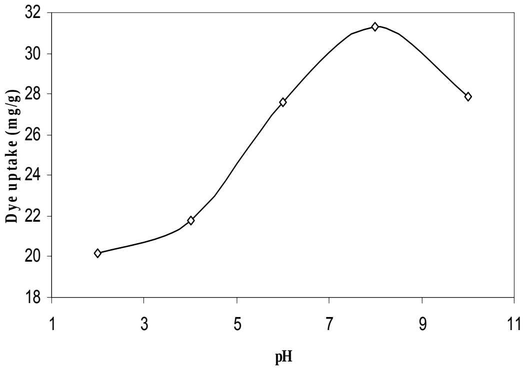
Optimum conditions for percentage color removal of malachite green dye using *Hydrilla verticillata* biomass were obtained by using RSM. Second order polynomial models obtained in this study were utilized for each response in order to determine the specified optimum conditions. The optimum values obtained by substituting the respective coded values of variables are: temperature-43.5°C, adsorbent dosage-0.26g, contact time-200min, adsorbent size 0.205mm (65mesh), and agitation speed-230rpm. At this condition the maximum percentage color removal was calculated.

The stationary point or central point is the point at which the slope of the contour is zero in all directions. The coordinates of the central point within the highest contour levels in each of these figures will correspond to the optimum values of the respective constituents. The maximum predicted color removal is indicated by the surface confined in the smallest curve of the contour diagram (8). The optimum values drawn from these figures are in close agreement with those obtained by optimizing the regression model Eq.(5).

The sequential quadratic programming in MATLAB 7 is used to solve the second-degree polynomial regression Eq. (5). The optimum values of the test variables were: temperature-43.5°C, adsorbent dosage-0.26g, contact time-200min, adsorbent size0.205mm (65mesh), and agitation speed-230rpm. The optimal values for the variables as predicted by MATLAB were found to be within the design region. This showed that the model correctly explains the influence of the chosen variables on the percentage color removal of Malachite green.

C. *Effect of pH*

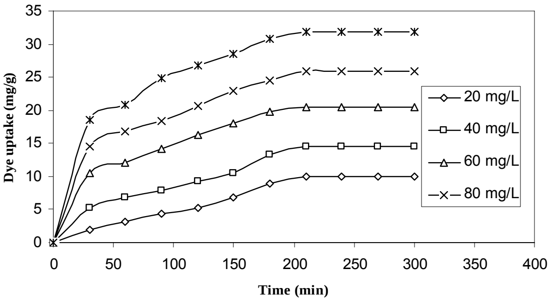
In this work, the effect of pH on the Malachite green adsorption onto Hydrilla verticillata biomass was studied in the range of 1-9. While the initial dye concentration, temperature, adsorbent dosage, contact time, particle size and agitation speed were fixed at 100 mg/l, 44°C, 0.26g, 200 min, 0.205mm and 230 rpm, respectively. Fig. 12 shows the effect of pH on the adsorption of MG by Hydrilla verticillata biomass. It can be seen that dye adsorption was unfavorable at pH < 4. The decrease in the adsorption with decrease in pH may be attributed to two reasons. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favour the adsorption of positively charged dye cations due to electrostatic repulsion. Secondly lower adsorption of MG at acidic pH is due to the presence of excess H+ ions competing with dye cations for the adsorption sites of the adsorbent [9]. This however, did not explain the slight decrease of dye adsorption at higher pH values. There might be another mode of adsorption (ion exchange or chelatation for example) [9]. Similar result was reported for the adsorption on methylene on cedar sawdust and crushed brick [9].



Fig, 12. Effect of pH on equilibrium uptake of MG using *Hydrilla verticillata.*

D. *Effect of initial dye concentration*

The effect of initial dye concentration on the malachite green adsorption onto *Hydrilla verticillata* biomass was studied in the range of 10-100 mg/l. The pH, temperature, adsorbent dosage, contact time, particle size and agitation speed were fixed at 8, 44°C, 0.26g, 200 min, 0.205mm and 230 rpm. The color removal profiles were obtained using the absorbance measurements. It was found that dye uptake increases with increasing dye concentration; it is shown in the fig .13.



Fig, 13. Effect of Initial dye concentration on equilibrium uptake of MG using *Hydrilla verticillata.*

E. Equilibrium isotherms

Two commonly used isotherms, Langmuir [10] and Freundlich [11], were employed in the present study. The nonlinear Langmuir and Freundlich isotherms are represented by Eqs. (6) and (7):

$$q_e = \frac{q_{\max} k_a C_e}{1 + k_a C_e} \qquad (6)$$

The values of q_o and k_L can be determined from the linear plot of C_e/q_e versus C_e. The Langmuir equation is used for homogeneous surfaces.

$$q_e = K_F Ce^{1/n} \qquad (7)$$

where C_e (mg/L) is the equilibrium concentration, q_e (mg/g) is the amount of dye adsorbed at equilibrium, and q_m (mg/g) and K_a (L/mg) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. K_F (mg/g) is the adsorption capacity and 1/n is a measure of the adsorption intensity.

The fitting of the experimental kinetic results to Eqs. (6) and (7) were done by nonlinear regression. The fitted results and the values of the estimated parameters are presented in Table 4. Fig. 14 shows the fitted equilibrium data in Freundlich and Langmuir isotherms. The fitting results, i.e. isotherm parameters and the coefficients of determination, R^2, are shown in Table 4. It can be seen in Fig. 14 that Freundlich isotherm fits the data better than Langmuir isotherm. This is also confirmed by the high value of R^2 in case of Freundlich (0.991) compared to Langmuir (0.963). The Malachite green biomass adsorbent used in this work had a relatively large adsorption capacity (91.92 mg/g) compared to some other adsorbents reported in the literature, such as bentonite clay (7.72 mg/g) [12] and arundo donax root carbon (8.70 mg/g) [13]. This indicates that Hydrilla verticillata biomass is effective for the removal of Malachite green from aqueous solutions.

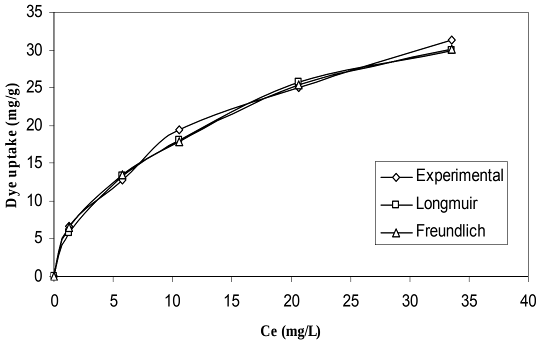


Fig. 14. Isotherm Plot for MG adsorption on to *Hydrilla verticillata*

F. *Kinetic modeling*

TABLE IV
ISOTHERM CONSTANTS AND KINETIC MODELS PARAMETERS FOR MG ADSORPTION ON *HYDRILLA VERTICILLATA*

Langmuir isotherm	
$q_{\max}$ (mg/g)	91.97
K_a (L/mg)	0.026
R^2	0.963
Freundlich isotherm	
K_f	3.17
n	1.299
R^2	0.991
Pseudo first order	
q_{exp} (mg/g)	35.66
q_e (mg/g)	31.79
R^2	0.969
Pseudo-second-order	
q_e (mg/g)	49.12
k_2 x 10^4	1.43
R^2	0.989

In order to investigate the mechanism of sorption and potential rate controlling steps, such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data of Malachite green aqueous solutions. When the biomass is employed as free and small-sized *Hydrilla verticillata* suspension in a well-agitated batch system, all the sorbent binding sites are readily available for the dye uptake.

Lagergren's pseudo-first-order model (Eq. (8)) [14], and Ho's pseudo-second-order model (Eq. (9)) [15] are

$$q = q_e\left(1 - e^{-k_1 t}\right) \qquad (8)$$

$$q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \qquad (9)$$

Where q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium, q (mg/g) is the amount of adsorbate adsorbed at time t, k_1 (L/min) is the rate constant of pseudo-first-order adsorption, k_2 (g/mg min) is the rate constant of pseudo-second-order adsorption

The fitting of the experimental kinetic results to Eqs. (8) and (9) were done by nonlinear regression. The fitted results and the values of the estimated parameters are presented in Table 4. The figures show that the straight line of log (1-(q/qe)) versus t suggests the applicability of this kinetic model. The plots in Figs. 15 demonstrate that the uptake, q, increases with increasing the initial concentration. It can be seen in Table 4 that the values of the coefficients of determination, R^2 of the pseudo- first-order model are higher than those of the pseudo second order model. The goodness of fit (fig. 15) and the accurate prediction of q_e both indicate that the pseudo-first-order model better describes the adsorption of Malachite green on *Hydrilla verticillata* biomass

TABLE V
RATE CONSTANTS FOR INTRA PARTICLE DIFFUSION OF MG ON TO *HYDRILLA VERTICILLATA*

C_o, mg/L	Acid blue 9	
		R^2
100	1.98	0.978

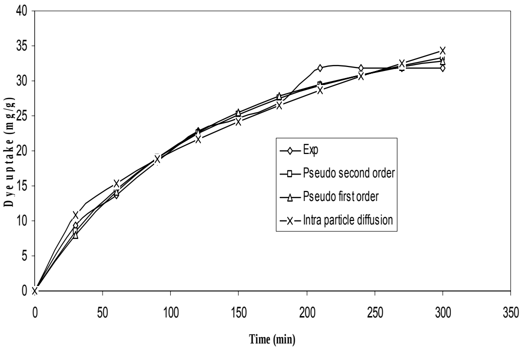


Fig. 15. Kinetic Plot for MG adsorption on to *Hydrilla verticillata*

G. *Intra particle diffusion*

In order to establish the possibility of the dye being transported with in the pores of the *Hydrilla verticillata*. The amount of Malachite green sorbed at optimum initial dye concentration 100mg/l on *Hydrilla verticillata* against the time of uptake ($t^{1/2}$) is investigated.

$$q_e = k_d t^{0.5} \tag{10}$$

All the plots had the same general features, an initial curve portion followed by linear portion. The rate constants for intra particle diffusion (k_d) are obtained from the slopes of the linear portion of the plots q versus $t^{1/2}$ from Fig. 20 for Malachite green. The k_d and R^2 values are listed in Table 5. The high R^2 value indicates the applicability of this model to our data. It shows that intra particle diffusion process took place.

IV. CONCLUSION

In this study, *Hydrilla verticillata* biomass, a cheap and widely available biomass is used for the removal of Malachite green from dilute aqueous solutions. The results obtained from the present investigation revealed the ability of *Hydrilla verticillata* biomass in removing Malachite green from aqueous solution. The maximum adsorption capacity was obtained (91.97 mg/g) at a solution pH ~8.0. From the kinetic and equilibrium studies it was found that pseudo II order kinetics and Freundlich isotherm fits the data well respectively. Although, further studies are needed in understanding the interaction behavior between the activated biomass and other dyes, the results indicate that *Hydrilla verticillata biomass* be employed as low-cost alternative to commercial materials in wastewater treatment for the removal of dyes.

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REFERENCES

[1]. K. Selvarani, "Studies on Low cost Adsorbents for the removal of Organic and Inorganics from Water," PhD, Thesis, Regional Engineering College, Tiruchirapalli. 2000

[2]. G. Sekaran , K.A. Shanmugasundaram, M. Mariappan, and K.V. Raghavan, "Adsorption of dyes by buffing dust of leather industry," *Indian J Chem Technol*, vol. 2, pp. 311-315, 1995.

[3]. S.D. Khattri, and M.K. Singh, "Colour removal from dye wastewater using sugar cane dust as an adsorbent," *Adsorpt Sci Technol*, vol. 17, pp. 269–282, 1999.

[4]. S.J. Culp, and F.A. Beland, "Malachite green: a toxicological review," *J Am College Toxicol*, vol.15, pp. 219–238, 1996.

[5]. M. Elibol, and D. Ozer, "Response surface methodological approach for inclusion of perfluorocarbon in actinorhodin fermentation medium," *Process Biochem*, vol. 38, pp. 667–773, 2002.

[6]. K. Umesh, M.P. Garg Kaur, and M.V. Garg Dhiraj Sud, "Removal of nickel[II] from aqueous solution by adsorption on agricultural waste biomass using a response methodological approach," *Bioresource Technology*, vol. 99, pp. 1325–1331, 2008.

[7]. G. Annadurai, R.S. Juang, and D.J. Lee, "Adsorption of heavy metals from water using banana and orange peels," *Water Sci Technol*, vol. 47, pp. 185–190, 2003.

[8]. M. Gopal, K. Pakshirajan, and T. Swaminathan, "Heavy metal removal by biosorption using Phanerochaete Chrysosporium," *Appl Biochem Biotechnol*, vol. 102, pp. 227–237, 2002.

[9]. O. Hamdaoui, "Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick," *J. Hazard. Mater*., vol. B135, pp. 264–273, 2006

[10]. I. Langmuir, "The constitution and fundamental properties of solids and liquids," *J. Am. Chem. Soc*, vol. 38 (11), pp. 2221-2295, 1913.

[11]. H. M. F. Freundlich, "Over the adsorption in solution," *Journal of Physical Chemistry*, vol. 57, pp. 385 - 470, 1906.

[12]. S.S. Tahir, and N. Rau, "Removal of a cationic dye from aqueous solutions by adsorption on to bentonite clay," *Chemosphere*, vol. 63, pp. 1842-1848, 2006

[13]. J. Zhang, Y. Li, C. Zhang, C. and Y. Jing, "Adsorption of malachite green from aqueous Solution onto carbon prepared from Arundo donax root," J.*Hazard. Mater*, vol. 150, pp. 774-782, 2008.

[14]. S. Lagergren, "About the theory of so-called adsorption of soluble substances," *K.Sven. Vetenskapsakad.Handl*., vol. 24(4), pp. 1-39, 1898.

[15]. Y.S. Ho, W.T. Chiu, and C.C. Wang, "Regression analysis for the sorption isotherms of basic dyes on sugarcane dust," *Bioresour. Technol*, vol. 96, pp. 1285– 1291, 2005.