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Removal of Methylene blue from aqueous solution by *Anthacephalous cadamba* based activated carbon: Process Optimization using Response Surface Methodology (RSM)

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Abstract: The unlimited discharge of dyes into the natural water bodies is a global environmental concern due to their toxic effects. Increasing environmental awareness is forcing waste creators to consider new options such as adsorption for the disposal of colored wastewaters. Due to prohibitive costs of commercially available activated carbon, low-cost adsorbents with high adsorption capacities have gained increasing attention. The present investigation deals with the adsorption of methylene blue on *Anthacephalous cadamba* leaf powder as activated carbon. The parameters pH, adsorbent dose and initial dye concentration considered in this investigation play an important role in the adsorption studies of MB dye removal. The optimum values of pH, adsorbent dose and initial dye concentration were found to be 10, 1g/L and 30 mg/L, for removal of MB dye, respectively. The experimental values were in good agreement with predicted values.
Keywords: Activated carbon, Adsorption, Methylene blue, Response surface methodology, *Anthacephalous Cadamba* leaf.

1. Introduction

India's dye industry manufactures different types of dyes, from which 50 % are reactive dyes. Large amounts of dyes are annually produced and used in textile, paper, pharmaceutical, cosmetics, food, leather and other industries[1,2]. Removal of these dyes from effluents in a cost- effective way remains as a major problem for textile industries[3]. The most commonly used methods for color removal are electro coagulation, ion exchange, irradiation, ozonation and advanced oxidation[4]. However, these processes are economic and effective only in cases where solute concentrations are relatively high. Many physicochemical methods have been tested, but adsorption is by far the most versatile and widely used method because of its ease of operation and low cost. Therefore, there is the need to look for low cost alternatives in easily available bio-materials such as peat[5], chitin[6], silica[7], Fugas saw dust [8], hardwood sawdust[9], hardwood[10], bagasse pith[11], mixture of flyash and coal[12], fly ash[13], chitosan fibre[14], rice husk[15], acid treated spent bleaching earth[16], slag[17], chitosan fibre[18-19], palm fruit bunch[20] , Bauhinia Purpuria leaves [21] and Chitosan modified Watermelon rind Composite[22] which can adsorb dyes from waste waters[23].

In this paper, we attempt to use activated carbon developed from *Anthacephalous* cadamba (AC) leaves, as an adsorbent for the removal of dyes from water. Since the AC leaves are available in GMR institute of technology, Rajam for free of cost, only the carbonization of its involved in the wastewater treatment. Therefore, it is a good adsorbent for the possibility of using dried AC leaves to develop a new low-cost activated carbon. The conventional method, changing one variable by keeping the other variables at a constant level does not give the effect of all the factors involved. Moreover, this method is time-consuming and also requires a large number of experiments to determine optimum levels, which may or may not be reliable. These problems can be eliminated by varying all the affecting parameters by using a statistical experimental design such as the response surface methodology (RSM)[24]. The present investigation is the utilization of the low-cost activated carbon, and the determination of the optimum conditions for Methylene blue (MB) dye removal from an aqueous solution using response surface central composite design methodology. The effect of experimental and their relations for the removal of MB were carried out by using CCD. The interactions between factors that influence the percentage of MB removal were established. The optimum value of the parameters was also determined for removal of MB from the aqueous solution using RSM.

2. Materials and methods

AC leaves as activated carbon, is used as adsorbent for dye removal. To get large surface area and to increase the porous capacity the adsorbent was completely activated.

2.1 Preparation of activated carbon from leaf powder

The objective of an activation process is to increase the volume and diameter of the pores. The leaves were washed, dried and powdered. The powder was carefully weighed and put in a beaker containing of chemicals such as $ZnCl_2$ and HCl.

The materials were mixed continuously to make it paste and heated to 600^0C for 2 hrs in a furnace and cooled to room temperature. Then the product was washed to make it to pH of 6 to7 and dried for 24 hrs at 90^0C.The powder was crushed and screened. The powder is taken for the experimental analysis.

2.2. Dye solution

A Stock solution of MB, concentration 1000 mg/L was prepared by dissolving 1gm of MB in 1000 ml of distilled water [25]. The range of concentration of prepared solutions varied between 10 and 50 ppm.

3. Experimental design

A standard response surface methodology (RSM) design known as central composite design (CCD) was used to study the influence of process parameters such as pH(X_1), dosage(X_2) and concentration(X_3) on the percentage removal of MB. Based on the ranges and the levels given, a complete design matrix of the experiments was employed as shown in Table 1. There are 8factorial points, 6 axial points and 6 replicates at the center points, indicated by a total of 20 experiments were employed in this study. The center points were used to verify the reproducibility of the data and the experimental error. The variables were coded to the (-1, 1) interval where low and high level were coded as -1 and 1, respectively. The axial points are located at (±a, 0, 0) (0, ±a, 0) and (0, 0, ±a) where a is the distance of the axial point from the center and makes the design rotatable. In this study, a value was fixed at 1.682 (rotatable). The response is MB removal efficiency (Y_1). It was used to develop an empirical model which correlated the response to the variables using a second degree polynomial equation. The optimum values of the test variables were obtained using the numerical point prediction tool in MINITAB (Version 16, PA, USA). The ‘‘prob [F’’ value of less than 0.05] indicates that the models significant[26-27]. It is desirable to indicate the influence of particular model terms that have significant effects on the response. Experimental conditions with the highest desirability were selected to be verified.

4. Results and discussion

4.1 Statistical analysis

The ultimate objective of CCD method used in this study was to find out the significant effects of the parameters *viz.* pH, initial concentration and adsorbent dosage and then to evaluate the optimum condition for MB removal from aqueous solution. Levels of selected variables are presented in Table 1. For statistical calculations, the variables X_i (the real value of an independent variable) were coded as X_i (dimensionless value of an independent variable) according to equation (1):$X_i = (X_i - X_0) / \Delta X$, Where X_0 is the value of X_i at the center point and ΔX represents the step change.

Table1. Experimental variables and levels investigated by central composite design

Variables		**Coded values**			
	-1.682	**-1**	**0**	**1**	**1.682**
pH (X_1)	4	8.81	10	11.18	12
Dosage (X_2, g/l)	0.06	0.076	0.1	0.12	0.14
Concentration (X_3, mg/l)	10	18.1	30	41.89	50

The experimental design matrix, the experimental results and the predicted dye removal efficiency are presented in Table 2.

Table 2: Experimental design matrix and results for adsorption of MB

Run	**Actual level of factors**			**Coded level of factors**			**% removal of MB**	
	X_1	X_2	X_3	X_1	X_2	X_3	%Removal	prediction
1	8.81	0.07	18.1	-1	-1	-1	86.2	85.15808
2	11.18	0.07	18.1	1	-1	-1	82	81.16808
3	8.81	0.12	18.1	-1	1	-1	91.8	91.12362
4	11.18	0.12	18.1	1	1	-1	86	86.11862
5	8.81	0.07	41.89	-1	-1	1	86.4	85.53384
6	11.18	0.07	41.89	1	-1	1	85.3	85.22884
7	8.81	0.12	41.89	-1	1	1	87.2	87.28438
8	11.18	0.12	41.89	1	1	1	85.67	85.96438
9	8.0	0.095	29.995	-1.68	0	0	86.5	87.62607
10	11.98	0.095	29.995	1.68	0	0	83.23	83.16091
11	9.995	0.052	29.995	0	-1.68	0	82	83.31105
12	9.995	0.137	29.995	0	1.68	0	89.2	88.94597
13	9.995	0.095	9.9900	0	0	-1.68	86.1	87.18535
14	9.995	0.095	49.999	0	0	1.68	87.4	87.37163
15	9.995	0.095	29.995	0	0	0	90.84	91.5314
16	9.995	0.095	29.995	0	0	0	91.75	91.5314
17	9.995	0.095	29.995	0	0	0	91.81	91.5314
18	9.995	0.095	29.995	0	0	0	92.32	91.5314
19	9.995	0.095	29.995	0	0	0	90.11	91.5314
20	9.995	0.095	29.995	0	0	0	92.54	91.5314

The behavior of the adsorption process is explained by the following empirical second-order polynomial model equation[28] (2):

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j$$

Where Y is the predicted response (dye removal efficiency), β_0 the constant coefficient, β_i the linear coefficients, β_{ii} the quadratic coefficients, β_{ij} the interaction coefficients and x_i, x_j are the coded values of the variables. MiniTab was used for the regression and graphical analyses of the data obtained. The reliability of the fitted model was justified through ANOVA and the coefficient of R^2.

$$Y=91.5314-X_1(1.32750)+X_2(1.67527)+X_3(0.0554)-X_1^2(2.17008)-X_2^2(1.91021)-X_3^2(1.50363)-X_1*X_2(0.253750)+X_1*X_3(0.921250)-X_2*X_3(1.05375)$$

Statistical regression coefficients for MB dye removal efficiency (%) are provided in Table 3. An amount of P ($P < 0.05$) for all independent parameters confirms that three selected factors are significant. However, it was found that all square and interaction terms except X_1^2 and X_2^2 (P values of 0.000) were insignificant to the response. The significance of each coefficient was evaluated by t test and p values, which are given in Table 3. The larger the magnitude of the t value and smaller the magnitude of the P value, the more significant is the corresponding coefficient [29-30]. Values of P less than 0.05 indicate the model term is significant. From the Table 3, the P values for solution pH, adsorbent dosage and initial dye concentration were found to be 0.001, 0 and 0.853. This implies that the linear effects of solution pH, adsorbent dosage and initial dye concentration are highly significant and influence the percentage of adsorption of the dye.

Table 3: Statistical regression coefficients for MB removal efficiency (%) in coded units

Term	Coef	SEcoef	T	P
Constant	91.5314	0.4392	208.407	0
X_1	-1.3275	0.2914	-4.556	0.001
X_2	1.6753	0.2914	5.749	0
X_3	0.0554	0.2914	0.19	0.853
X_1^2	-2.1701	0.2837	-7.65	0
X_2^2	-1.9102	0.2837	-6.734	0
X_3^2	-1.5036	0.2837	-5.301	0
X_1*X_2	-0.2537	0.3807	-0.666	0.52
X_1*X_3	0.9212	0.3807	2.42	0.036
X_2*X_3	-1.0537	0.3807	-2.768	0.02

ANOVA for the selected dye removal is also listed in Table 4. In this case, the P-value of 0.000 ($P < 0.05$) for regression model equation implies that the second-order polynomial model fitted to the experimental results as well. The lack-of-fit was also calculated from the experimental error (pure error) and residuals. "F-value of Lack-of-fit" of 1.72 implies the significance of model correlation between the variables and process response for dye removal. Additionally, the value of R^2 =0.9282 confirm the accuracy of the model. Furthermore, the parity plot for the experimental and predicted value of MB removal efficiency (%) is demonstrated in below Fig.1.

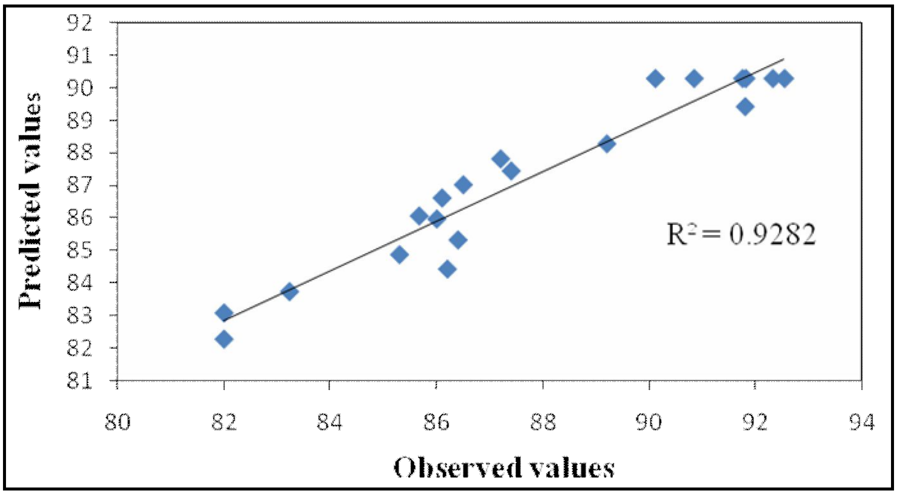

Fig.1 Parity plot for MB adsorption

The adequacy and significance of second order response surface models were further tested by the analysis of variance (ANOVA). The ANOVA summary is given in Table 4. ANOVA gives the information about quadratic and interaction effects along with the normal linearized effects of the independent variables. The statistical significance of model equations was determined by the F-test. The significance of each coefficient was evaluated by F-values and P-values. The larger fisher F- value with a low probability value (<0.05) demonstrate that the developed mathematical models were fitted well to the experimental data. From the ANOVA results, it is evident that the main and square effects were highly significant in comparison with interaction effects.

Table 4: ANOVA results for MB removal efficiency (%)

Source	DF	SeqSS	AdjMS	F	P
Regression	9	207.201	23.0223	19.85	0
Linear	3	62.437	20.8124	17.95	0
X_1	1	24.067	24.0668	20.75	0.001
X_2	1	38.328	38.3283	33.05	0
X_3	1	0.042	0.0419	0.04	0.853
Square	3	128.576	42.8587	36.96	0
X_1^2	1	50.862	67.8661	58.52	0
X_2^2	1	45.132	52.5857	45.35	0
X_3^2	1	32.582	32.5825	28.1	0
Interaction	3	16.188	5.3959	4.65	0.028
X_1*X_2	1	0.515	0.5151	0.44	0.52
X_1*X_3	1	6.79	6.7896	5.85	0.036
X_2*X_3	1	8.883	8.8831	7.66	0.02
Residual Error	10	11.596	1.1596		
Lack-of-fit	5	7.339	7.339	1.72	0.282
Pure Error	5	4.257	0.8515		
Total	19	218.797			

The response surface plots and contour plots estimate the % RE of MB onto activated carbon over independent variables of initial solution pH, initial concentration and the adsorbent dosage. The response surface plots as a function of two variables at a time, maintaining all other variables at fixed levels is more useful in understanding both the main and the interaction effects of these two variables.

Fig. 2 shows the interactive effect of concentration and dosage by keeping the pH at their optimum values. Similarly, remaining surface plots explain the interaction effects of other independent variables on percentage of adsorption of dyes. It is evident from the Fig. 2 to 7 that the percentage of adsorption was increased with an increase in adsorbent dosage and initial dye concentration of the dye[31].

4.2. Response surface plots and contour plots

Surface and contour plots demonstrate the effects of different process parameters (two parameters varied at a time while the third parameter is maintained at the middle level) on the % RE of MB (shown in Fig. 2 to 7). The stationary points were examined by analyzing these plots. In general, circular contour plots indicate that the interactions between parameters are almost negligible while the elliptical ones indicate the evidence of the interactions.

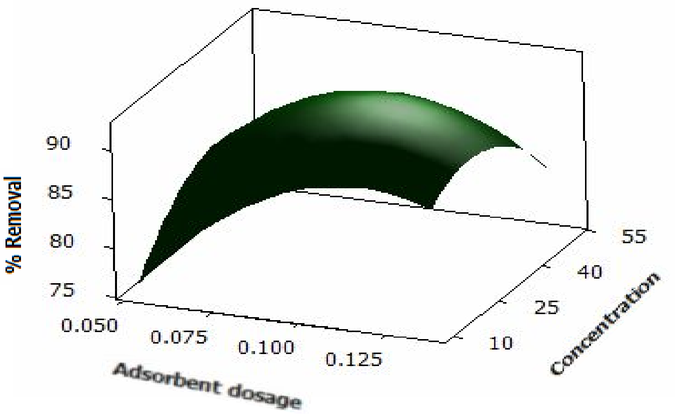

Figure.2. Surface plot showing the interactive effect of dosage and concentration on MB

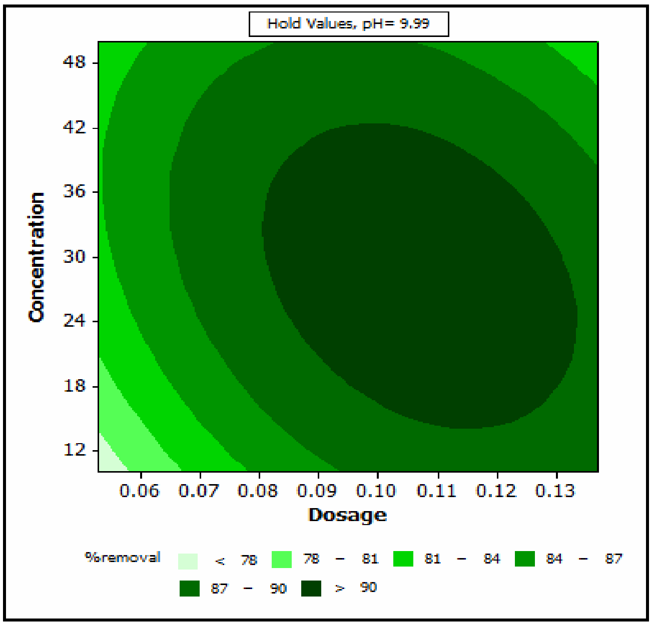

Figure.3. Contour plot showing the interactive effect of dosage and concentration on MB

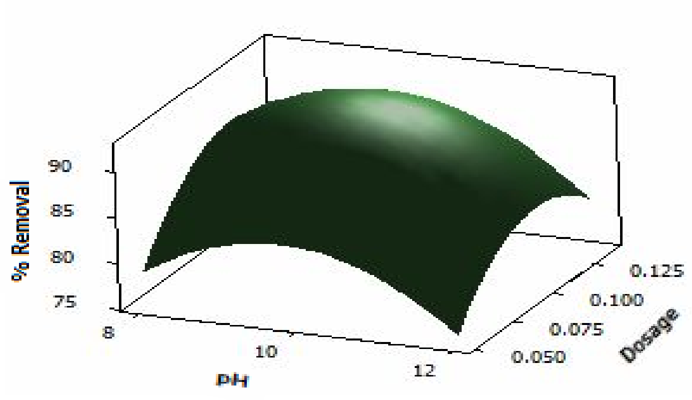

Figure.4. Surface plot showing the interactive effect of dosage and pH on methylene blue

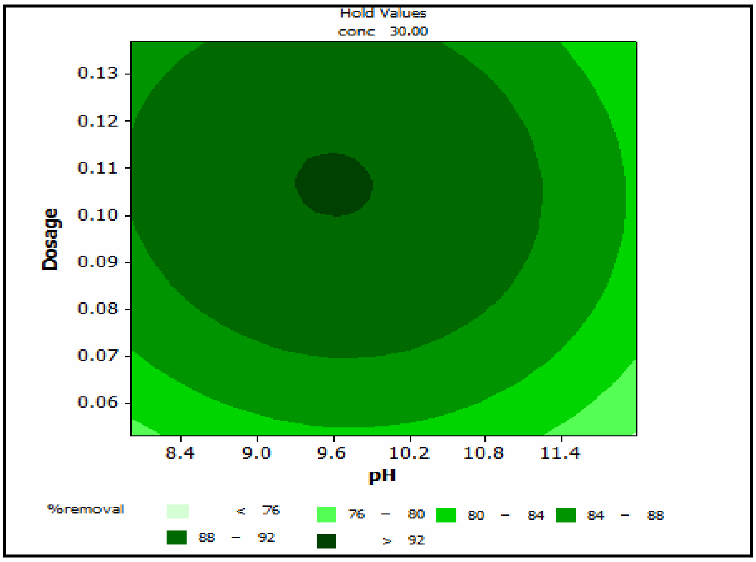

Figure.5. Contour plot showing the interactive effect of dosage and pH on MB

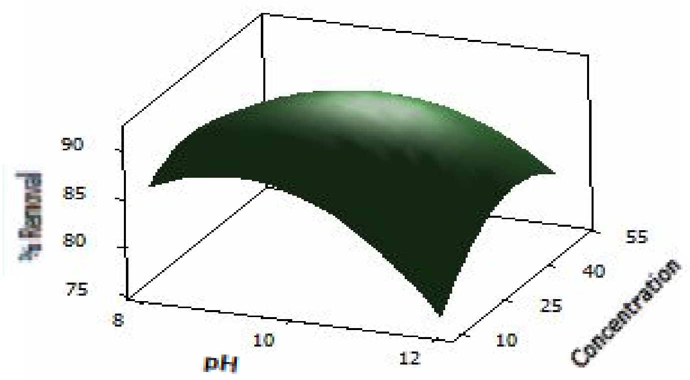

Figure.6. Surface plot showing the interactive effect of pH and concentration on MB

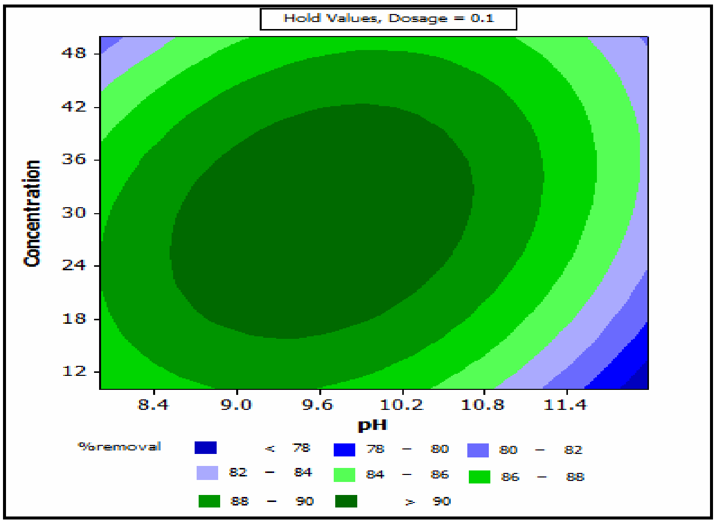

Fig.7. Contour plot showing the interactive effect of concentration and pH on MB

The Figures 4 and 6 showed the effect of pH in the % RE of MB. The maximum removal is obtained at pH of 10. It was found that at low pH, the dyes become protonated, the electrostatic repulsion between the protonated dyes and positively charged adsorbent sites results in decreased adsorption. Higher adsorption at increased pH may be due to increased protonation by the neutralization of the negative charges on the surface of the adsorbent; which facilitates the diffusion process and provides more active sites for the adsorbent[32-33].

It can be observed from the Figures 2 and 4, the % removal of MB on ACLAC was increased with the increasing of adsorbent dosage from 0.06g until 0.1 g (92.54%). The increase of the removal of MB is due to the increase of the adsorbent surface area and availability.

From the Fig. 2 and 6 the adsorption percentage decreases and the extent of adsorption increase with increasing initial dye concentration. This is obvious from the fact that the initial MB concentration provides an important driving force to overcome all of mass transfer resistance. Furthermore, the increase of loading capacity of ACLAC with increasing initial MB concentration may be due to higher interaction between MB and adsorbent. For constant dosage of adsorbent, at higher initial concentrations, the available adsorption sites of adsorbent became fewer and hence the removal of MB depends upon the initial concentration[33].

According to the results it was observed that there was an increase in the dye removal efficiency, with an increase in the initial pH and adsorbent dose. And with an increase in the initial dye concentration, there was a decrease in the dye removal efficiency. The effect of the three selected independent parameters and interactions among the RSM were analyzed which showed that some interactions like ($X_1^2X_2^2$ and X_3^2) effected the adsorption performance as well as all the selected parameters. The ANOVA showed a high R^2 (0.9282) value of the regressions model equation, showing a satisfactory adjustment of the second-order regression model with the experimental data[34]. The optimum MB removal efficiency was found at an initial pH of 10, adsorbent dose of 0.1g, and initial dye concentration of 30 mg/l. An experiment was accomplished in optimum conditions which confirmed that the model and experimental results are in close agreement (92.54% compared to 90.54% for the model).

6. Conclusions

The biomass of AC leaves as activated carbon demonstrates a good capacity of biosorption of MB, highlighting its potential as an effective biosorbent for the treatment of industrial effluent. This study clearly shows that the response surface methodology is one of the suitable methods for optimization of process parameters to maximize the dye removal. The statistical analysis results proved the significance of the model developed from experimental data to optimize the parameters. The optimum values of pH, adsorbent dose and initial dye concentration were found to be 10, 0.1 g and 30 mg/L, for complete removal of MB dye, respectively. The experimental values were in good agreement with the 2nd order polynomial model predicted values. From the results it can be concluded that AC leaves can be effectively utilized for the treatment of industrial wastewater.

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