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Research Paper

Utilization of Corn Cob Activated Carbon for Adsorptive Removal of MB Dye from Aqueous Solution: Application of RSM approach in Optimization of Removal Process

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Abstract: *Corn cob activated carbon (CCAC) was prepared and characterized by SEM, BET and FTIR spectroscopic techniques and employed as adsorbent for removal of Methylene blue (MB) dye from aqueous solution. Response surface methodology (RSM) combine with three-level, four-variable, Box–Behnken design (BBD) was used to optimize the individual and interactive effect of four different experimentally controlled environmental factors like temperature, initial pH of solution, MB dye concentration and adsorbent dose on removal efficiency. Adequacy of the developed model was evaluated by statistical method. The removal capacity of CCAC for MB dye from aqueous solution predicted by model (166.6 mg g^{-1} , MB) was in good agreement with experimental value (166.7 mg g^{-1}, MB) under the optimum conditions of process variables. The results of the study indicate that CCAC can be used for effective removal of MB dye from water contaminated with MB dye.*

Keywords: Box- Behnken design, Response surface modeling, Adsorption, Process optimization, Methylene blue dye, Corn cob activated carbon.

Introduction

Textile industry is one of the largest producers of industrial wastewater with high color and dissolved organic compounds including variety of dyes and chemicals that make it an environmental challenge. Most of the pollution in textile wastewater is a result of dyeing processes [1, 2]**.** At present, more than 1,00,000 different dyes amounting nearly 30 million tons are commercially produced and synthesized, which are commonly used in textile, paper, leather, plastics and other industries. These dyes can be classified according to ionic property or on the basis of the chemical structures of their particular chromophoric group [3]. The growth rate of production and subsequent consumption of dyes is increasing gradually reflecting enhanced environmental pollution [4, 5]. The presence of small amount of dyes is visible in textile wastewater and undesirable in terms of color [6]. Discharged colored wastewater influences the aquatic system [7, 8, 9]. Besides imparting color into wastewater, the dyes are toxic and even carcinogenic and these pose a serious hazard to aquatic living organisms [10]. Color impedes light penetration, retards photosynthetic activity and inhibits the growth of biota. Water soluble dyes are considered to have poor biodegradability and it is estimated that about 20% of the total dye remains in the wastewater during the production process [11]. The contamination of drinking water by dyes even at a concentration of 1.0 mg L^{-1} could impart significant color, making it unfit for human consumption [12].

Methylene blue (MB), is a synthetic cationic dye is predominantly used in textile industries. Being a cationic dye, it is important to control and treat MB as cationic dyes are more toxic compared to the anionic dyes [13]. MB can easily combine with negatively charged cells membrane surfaces, and can penetrate into cells and got concentrated in cytoplasm [14]. It is also responsible for hypertension, precordial pain, dizziness, mental confusion, headache, fever, staining of skin, injection site necrosis, faecal discoloration, nausea, abdominal pain, discoloration of urine, bladder irritation and anaemia [15, 16]. Therefore, it is important to remove the dyes, particularly MB, from wastewater before discharge.

In recent years several physical and chemical processes like that biological oxidation, chemical coagulation, advanced oxidation process and adsorption are used in the treatment of wastewaters containing color organic compounds. Most of the dyes are resistant to be decolorized by chemicals, heat and light due to their complex chemical structures [17]. The biodegradation of dyes is a typically slow and undesired process. However among these methods adsorption on activated carbon (AC) is the mostly applied method for the removal of dyes from wastewaters, because of their high porous structure and high surface area. Although adsorption processes are very effective, but commercially available activated carbons are expensive and have greater the cost. In view of adsorbent cost and availability, the agricultural wastes are now considered as good choice in the preparation of low cost adsorbent. Moreover disposal of agricultural by- products is currently a major economic and ecological issue, that's why the conversion of agricultural wastes in to environment friendly, effective and of low cost adsorbents, such as, AC, represents a meaningful utilization of agricultural waste materials. Recently various agricultural wastes such as pistachio shell [18], Trapa natans husk [19], walnut shells [20] have been used to derive AC. Like that all the above agricultural wastes corn cob is also generated significantly all around the world. The annual production worldwide is about 520x10^9 kg [21]. Asia is the second major production region. In India, the annual production was about17,300,000 tons in 2009 [22]. The corn cob is the waste generated during processing corn. Since the ratio between corn grain and corn cob may reach 100: 18, thus a large quantity of corn cob was generated.

In this study AC was prepared by using corn cob (CC) and their (CCAC) applicability was investigated as an adsorbent for methylene blue (MB) dye from aqueous solution. The effects of most influencing parameter such as contact time, initial concentration MB dye, temperature, dose of adsorbent and initial pH were investigated in MB dye removal process from aqueous solution. In another part of this study, response surface methodology (RSM) combining Box-Behnken Design (BBD) was used to study the individual and combined effect of four process variables i.e. temperature , initial solution pH, initial MB dye solution and CCAC dose on adsorptive removal of MB dye from aqueous solution. The present study was aimed to develop mathematical model and study the interactive effect of process variables as well as maximizing the removal MB dye from aqueous solution using optimization of process variables.

Material and Methods

All reagents and chemicals used in the study were of analytical reagent grade. Methylene Blue dye (C.I. 52015, $C_{16}H_{18}N_3SCl$, mol. wt. 319.85, IUPAC name3,7- bis (Dimethylamino)- phenothiazine- 5- ium chloride (aq. Solubility 40 g L^{-1}) with the chemical structure (Fig. 1) was procured from M/s Merck, India. The stock solutions of the dye were prepared as required by serial dilution of the stock solution in distilled water.

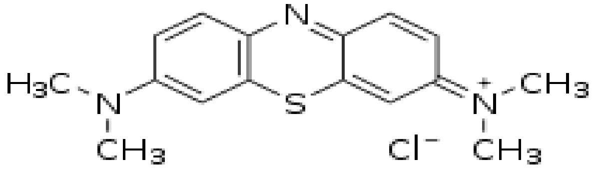


Figure 1: Chemical structure of Methylene Blue dye in neutral medium

Adsorbent development

Corn cob was obtained from the local market in Lucknow, India. Corn cob was firstly washed with water and subsequently dried at 105ºC for 24 h to remove the moisture content. The dried corn cob was crushed and sieved to the size of 1-2 mm. Carbonization procedure was carried out at 700ºC for 2 h under purified nitrogen (99.99%) flow of 150 mL min^{-1} [23]. The char produced was mixed with Na_2CO_3 pellets in 1:1. Deionised water was added to dissolve all the Na_2CO_3 pellets. The mixture was then dehydrated in an oven at 110ºC for 24 h to remove moisture.

After dehydration, the sample was placed in electric furnace for activation step. Once the final activation temperature (758°C) was reached, the gas flow was switched from nitrogen to CO_2 at flow rate of 150 mL min^{-1} for different period of time. The sample was then cooled to room temperature under nitrogen flow. Then the sample was dried in an oven at 110°C for 6 h. The product was sieved to the desired particle size and finally, stored in vaccum desiccators until required. The developed carbon was designated as the corn cob activated carbon (CCAC).

Adsorbent characterization

The chemical constituents of the prepared corn cob activated carbon were determined following the methods reported elsewhere [24]. The elemental analysis was performed using the Elemental Analyser model Vario EL-III (Hanau, Germany). The BET specific surface area (S_{BET}), was determined by N_2- physiosorption using the surface area analyser model Autosorb- 1C (Quantachrome, USA). Scanning electron microscopy (SEM) characterization was performed by SEM model LEO 430 (Cambridge, England) [25]. The identification of surface functional group on CCAC was performed using an FTIR spectrometer (Perkin- Elmer FTIR model RX1, USA) in the range 4000- 450 cm^{-1}. The point of zero charge (pH_{ZPC}) of CCAC surface was determined by using the solid addition method [26].

Table 1: BBD matrix with four independent variables (actual. A and coded, C values) and corresponding experimental and predicted removal (in mg g^{-1}) of MB dye

S. No.	Temperature(^{0}C)		pH		Concentration (mg L^{-1})		Dose (g L^{-1})		Adsorption (mg g^{-1})	
	A	C	A	C	A	C	A	C	Experimental	Predicted
1	20	-1	4	-1	200	0	0.7	0	105.87	104.52
2	20	-1	9	1	200	0	0.7	0	110.97	112.4
3	50	1	4	-1	200	0	0.7	0	152.64	149.68
4	50	1	9	1	200	0	0.7	0	157.74	157.56
5	35	0	6.5	0	150	-1	0.4	-1	131.70	138.79
6	35	0	6.5	0	250	1	0.4	-1	142.86	137.69
7	35	0	6.5	0	150	-1	1	1	143.75	147.39
8	35	0	6.5	0	250	1	1	1	155.95	147.33
9	20	-1	6.5	0	150	-1	0.7	0	107.99	102.35
10	20	-1	6.5	0	250	1	0.7	0	97.79	104.33
11	50	1	6.5	0	150	-1	0.7	0	159.44	150.07
12	50	1	6.5	0	250	1	0.7	0	144.13	146.93
13	35	0	4	0	200	0	0.4	-1	141.37	132.57
14	35	0	4	0	200	0	1	1	147.02	141.69
15	35	0	9	0	200	0	0.4	-1	157.74	132.57
16	35	0	9	0	200	0	1	1	151.19	141.69
17	20	-1	6.5	0	200	0	0.4	-1	105.65	108.22
18	20	-1	6.5	0	200	0	1	1	110.12	106.56
19	50	1	6.5	0	200	0	0.4	-1	134.67	142.6
20	50	1	6.5	0	200	0	1	1	160.71	162.5
21	35	0	4	0	150	-1	0.7	0	137.33	133.37
22	35	0	4	0	250	1	0.7	0	137.76	132.79
23	35	0	9	0	150	-1	0.7	0	146.68	133.37
24	35	0	9	0	250	1	0.7	0	144.98	132.79
25	35	0	6.5	0	200	0	0.7	0	127.55	127.41
26	35	0	6.5	0	200	0	0.7	0	126.70	127.41
27	35	0	6.5	0	200	0	0.7	0	127.98	127.41

Adsorption experiment

Adsorption experiments were conducted by transferring 25 ml of solution with three different MB dye concentration (150, 200, and 250 mg L^{-1}) and CCAC dose (0.4, 0.7, and 1.0 g L^{-1}) to 50 mL conical flasks at three different pHs (4.0, 6.5, and 9.0) and temperatures (20, 35 and 50 °C). The pH of the test solution was adjusted using reagent grade dilute hydrochloric acid and sodium hydroxide. The sorption experiments were conducted in a thermo- controlled (±1ºC) water bath shaker for 90 min at 120 rpm. At the end of each experiment, samples were withdrawn, centrifuged and supernatant was suitably diluted for analysis of rest dye concentration after adsorption process. The residual concentration of the dye in the solution was then determined using the UV- vis spectrophotometer at 663 nm (λ_{max} of the dye). The adsorption (mg g^{-1}) of the dye by the adsorbent was calculated as [25],

$$\mathbf{q_e = (C_o - C_e)V / W} \qquad (1)$$

where C_o and C_e are the initial and final concentrations (mg L^{-1}) of the dye in solution, respectively. The V and W represent the solution volume and adsorbent weight (g) respectively. All sorption experiments were performed in duplicate and the mean of the two are taken for all calculations. The experimental conditions and the corresponding dye adsorption (mg g^{-1}) measured through the batch experiments are presented in Table 1.

Experimental design and optimization

In the present study response surface methodology (RSM) combining with three levels, four factorials Box-Behnken experimental design was applied for investigating and validating the process variables. The experimental ranges of the operating temperature and initial pH of the solution were chosen on the basis of the present environmental conditions [27]. The most influencing process variables for dye removal, namely temperature (X_T), initial pH of solution (X_{pH}), initial dye concentration (X_{Co}) and adsorbent dose (X_D) were selected as independent variables on the basis of preliminary experiment and removal of dye in mg g^{-1} (Y) was considered as dependent variables (response). The selected process variables with their limits, units and notations are given in Table 2. In this study total 27 experiments were runs including three replicates at center points. The Design Expert 8.1 (trial version) software was used to analyze the experimental data and regression & graphical analysis.

In the optimization process, the response (removal efficiency of CCAC) can be simply related to the chosen factors by quadratic models. Quadratic models for predicting optimal point is given below as Eq. 2.

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_1^2 + \sum_{i=1}^{n} \sum_{j=1}^{n} \beta_{ij} X_i X_j + e \quad \ldots \qquad (2)$$

where Y is the predicted response, 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 independent process variables, and e is the residual error.

Table 2: Process control variables, their coded values and limits

Variable	Unit	Notation	Limits			Step change value, (ΔX_i)
			-1	0	+1	
Temperature	°C	T	20	35	50	15
Initial pH of solution	-	pH	4	6.5	9	2.5
Initial concentration of dye	mg L^{-1}	C_0	150	200	250	50
Adsorbent dose	g L^{-1}	D	0.4	0.7	1	0.3

Table 3: Coded factor levels for BBD matrix for optimization involving four variables (X_1, X_2, X_3 and X_4)

X_1	X_2	X_3	X_4
±1	±1	0	0
0	0	±1	±1
0	0	0	0
±1	0	0	±1
0	±1	±1	0
0	0	0	0
±1	0	±1	0
0	±1	0	±1
0	0	0	0

The analysis of variance (ANOVA) and the *t* test statistics are used to check the adequacy of the model and statistical significance of the regression coefficients [28]. The measured and the model predicted values of the response variable were used to calculate the coefficient of determination (R^2), the root mean square error of prediction (RMSEP), and the relative standard error of prediction (RSEP). The correlation between the measured and predicted values indicates the goodness of fit of the model, whereas the RMSEP and RSEP values are used to assess the predictive ability of the selected model.

Optimization modeling

The optimization of dye removal was performed to select the levels of the independent variables for maximum removal of dye from aqueous solution. The identified quadratic model was used to optimize the process variables within their experimental ranges for the dye removal.

Desorption experiment

Desorption of MB dye from the activated carbon was investigated to study the interaction between the adsorbate and adsorbent. First adsorption of dye (200 mg L^{-1}) on activated carbon (0.4 g L^{-1}) was conducted at pH 6.97 and temperature 30°C for 1.5 h. After 1.5 h, the dye adsorbed activated carbon was centrifuged, separated and gently washed with distilled water to remove any unadsorbed dye molecules trapped between the adsorbent particles. Next, the desorption was carried out separately in 25 ml of (a) 0.1 M NaOH and (b) 0.1 M HCl for 12 h. The concentration of dye adsorbed/ desorbed was estimated by recording absorbance at wavelength of 663 nm.

Results and Discussion

Characterization of the adsorbent

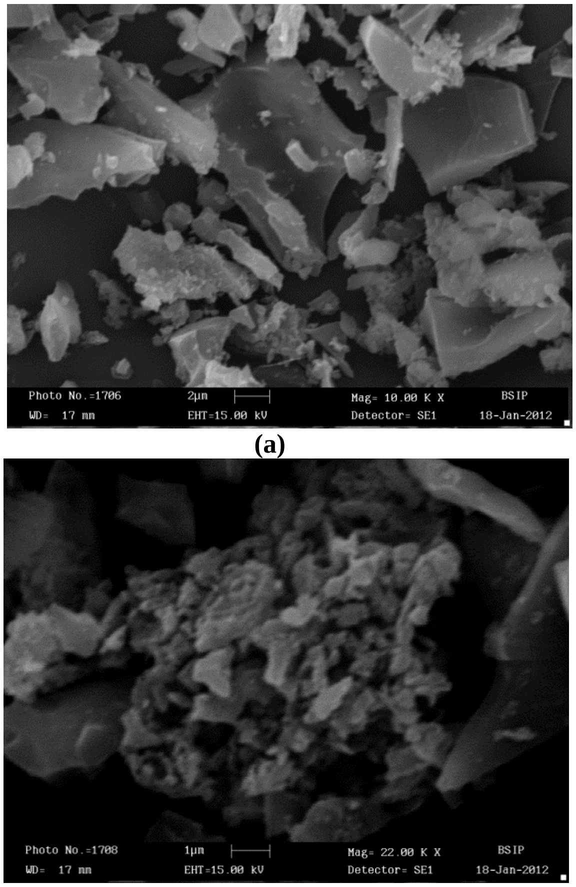
The chemical composition and surface properties of the developed corn cob activated carbon are listed in Table 4. This indicated that the CCAC has a high specific surface area.

Table 4: Composition and surface properties of the corn cob activated carbon

C(%)	H(%)	N(%)	S_{BET}(m^2 g^{-1})	V_T(cm^3 g^{-1})	pH_{zpc}
56.65	0.01	0.1	498.02	0.2880	7

S_{BET} = surface area, V_T = total pore volume

The FTIR spectra of CCAC (figure not shown due to brevity) showed weak and broad peaks in the region of 3420-525 cm^{-1}. FTIR spectra shows peak at 3420 cm^{-1} due to presence of O-H and N-H stretching vibration, while peak at the 2921 cm^{-1} is attributed to the C-H group of alkyl chain. The 1559-1018 cm^{-1} band was assigned to the C-O stretching and O-H bending modes such as phenolic and carboxylic acids. The spectral analysis shows the heterogeneous nature and scanning electron microscopic (SEM) photograph (Fig 2a and 2b) revealed the coarse and rough morphology of the corn-cob activated carbon surface.



(a)

(b)

Figure 2a and 2b: Scanning Electron Micrograph (SEM) of activated carbon

Response surface quadratic model

Results obtained by performing batch experiment according to the BBD matrix for adsorbtive removal of MB from aqueous solution are presented in Table 2. The quadratic model equation relating the adsorption efficiency of CCAC for dye removal to the independent removal process variables in terms of the coded variables as developed by software is given by following Eq.

$$Y\ (mg/g) = 127.41 + 22.58 X_T - 7.16 X_T^2 + 3.94 X_{pH} + 10.79 X_{pH}^2 - 0.29 X_{Co} + 5.67 X_{Co}^2 + 4.56 X_D + 9.72 X_D^2 + 0.000 X_T X_{pH} - 1.28 X_T X_{Co} - 0.53 X_{pH} X_{Co} + 5.39 X_T X_D - 3.05 X_{pH} X_D + 0.26 X_{Co} X_D \quad (3)$$

The statistical significance of the response surface quadratic model was tested by using analysis of variance (ANOVA). The results of ANOVA concluded that model was highly significant, as it is can be justify by the Fisher's F value (13.19) with a low probability value (<0.0001).

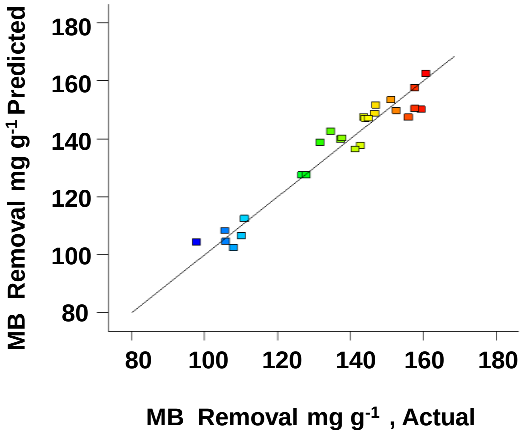


Figure 3: Plot of the actual and model predicted adsorption (mg g^{-1}) of the MB dye for the model development

A fairly high value of the correlation coefficient (R^2 = 0.987) between the experimental and model predicted values of the response variable implies that this developed quadratic model was statistically significant and it cannot explain only 0.013 % of the total variations. The R^2 value also shows good agreement with the adjusted correlation coefficient (adj. R^2 = 0.9690). Thus overall analysis of ANOVA implies the applicability of the developed model to predict the response (removal efficiency of CCAC for MB dye removal from aqueous solution) within the limit of process variables, as well as high correlation (R^2 = 0.987) among the predicted and the measured values of the response factor and considerably low RMSEP (7.76) and RSEP (5.66) values signifying that model is highly significant and experiments are highly accurate and reliable.

Table 5:The ANOVA results for the response surface quadratic model for adsorption of the MB dye

Source	Coefficient	Sum of Squares	DF	Mean Squares	F- value	p- value	Remarks
Intercept	127.41	8587.77	14	613.41	13.19	<0.0001	significant
X_T	22.58	6117.36	1	6117.36	131.56	<0.0001	significant
X_{pH}	3.94	186.61	1	186.61	4.01	0.0683	
X_{Co}	-0.29	0.98	1	0.98	0.021	0.8872	
X_D	4.56	249.91	1	249.91	5.37	0.0389	significant
X_T^2	-7.16	273.26	1	273.26	5.88	0.0321	significant
X_{pH}^2	10.79	620.57	1	620.57	13.35	0.0033	significant
X_{Co}^2	5.67	171.56	1	171.56	3.69	0.0788	
X_D^2	9.72	503.75	1	503.75	10.83	0.0064	significant
X_TX_{pH}	0.000	-1.819E-012	1	-1.819E-012	-3.912E-014	1.0000	
X_TX_{Co}	-1.28	6.51	1	6.51	0.14	0.7149	
$X_{pH}X_{Co}$	-0.53	1.13	1	1.13	0.024	0.8787	
$X_T X_D$	5.39	116.40	1	116.40	2.50	0.1396	
$X_{pH} X_D$	-3.05	37.22	1	37.22	0.80	0.3885	
$X_{Co} X_D$	0.26	0.27	1	0.27	5.834E-003	0.9404	
Residual		557.99	12	46.50			
Lack of fit		557.14	10	55.71	132.09	0.0075	significant
Pure error		0.84	2	0.42			
Total		9145.76	26				

DF degrees of freedom

Effects of model components and their interactions on dye adsorption

Significance of each coefficient of Eq. (3) was determined by applying t-test and p-values of each parameter (Table 5 and 6). The *p* value is used as a tool to check the significance of the coefficient [29]. The linear effects of coefficients Temperature (X_T), and dose are significant, while initial pH of the solution and dye concentration are insignificant. The quadratic effect of temperature, initial pH of the solution and dose of CCAC are also found significant.

Table 6: Multiple regression results and significance of the components for the quadratic model

Factor (coded)	Parameter	Coefficient	Effect	t- value	Sum of squares	PC
Intercept	β_0	127.41	254.82	129.350	8587.77	-
X_T	B_1	22.58	45.16	45.847	6117.36	73.83
X_T^2	B_2	-7.16	-14.32	-9.708	273.26	3.29
X_{pH}	B_3	3.94	7.88	8	186.61	2.25
X_{pH}^2	B_4	10.79	21.58	14.630	620.57	7.48
X_{Co}	B_5	-0.29	-0.58	-0.588	0.98	0.01
X_{Co}^2	B_6	5.67	11.34	7.688	171.56	2.07
X_D	B_7	4.56	9.12	9.258	249.91	3.01
X_D^2	B_8	9.72	19.44	13.179	503.75	6.07
$X_T x X_{pH}$	B_9	0.000	0	0	-1.819E-012	-2.19539E-14
$X_T x X_{Co}$	B_{10}	-1.28	-2.56	-1.501	6.51	0.07
$X_{pH} x X_{Co}$	B_{11}	-0.53	-1.06	-0.621	1.13	0.01
$X_T x X_D$	B_{12}	5.39	10.78	6.322	116.40	1.40
$X_{pH} x X_D$	B_{13}	-3.05	-6.1	-3.577	37.22	0.44
$X_{Co} x X_D$	B_{14}	0.26	0.52	0.304	0.27	0.003

The percent contribution (PC) of each of the individual term in final model were computed (Table 6) using the SS values of the corresponding term. The PC of a term is obtained as the ratio of SS of an individual term to that of sum of SS for all the terms [30] (Yetilmezsoy et al 2009), as;

$$\mathbf{PC} = \frac{SS}{SS}\ \mathbf{x\ 100} \qquad (4)$$

As evident from Table 6, the temperature (X_T) showed the highest level of significance with a contribution of >74% as compared to other components.

Three- dimensional response surface plots

In order to investigate and visualize the interaction among the different independent variables and their corresponding effect on dye removal efficiency of the CCAC three dimensional response surface plots were constructed. (Figs. 4a- c and 5a- c). These plots can be helpful in understanding both the main and interaction effects of variables of removal process on the removal efficiency of CCAC [31].

Effect of temperature and Ph

In adsorption process, both the temperature and solution pH play very important role. These variables are considered to be most effective in influencing the sorption process. Fig. 4a shows the three- dimensional response surfaces representing the combined effect of temperature and pH on adsorption of the dye at constant initial dye concentration (200 mg L^{-1}) and adsorbent dose (0.4 g L^{-1}). The dye sorption increases with both the solution pH and temperature within their respective experimental ranges. Such temperature- dependence may be attributed to either relatively higher affinity of the sites for dye or an increased number of the binding sites in the adsorbent with increase in temperature [32]. The pH- dependence of dye adsorption on CCAC may be explained in terms of the solution pH and pH_{ZPC} of the adsorbent. At solution pH< $pH_{ZPC,}$ a relatively higher number of negatively charged sites on adsorbent surface enhances the sorption of dye [33]. A maximum adsorption of dye (>181 mg g^{-1}) was determined at constant concentration (200 mg L^{-1}) and adsorbent dose (0.4g L^{-1}).

Effect of temperature and initial dye concentration

The interactive effect of process temperature and initial concentration of the dye in solution on the adsorption by the prepared CCAC at constant pH (6.9) and dose (0.4g L^{-1}) is shown in Fig. 4b. It is evident that dye adsorption shows a declining trend with increasing concentration in the solution and increased with process temperature. This behavior can be understood as the increasing adsorbate concentration with fixed adsorbent dose would result in saturation of the binding sites on the surface at lower temperature and subsequently declining of the adsorbate uptake with increasing concentration, whereas, at higher temperature, the number of binding sites increases, hence enhancing the sorption process. A maximum dye removal (>181 mg g^{-1}) was determined at constant pH (6.9) and adsorbent dose (0.4 g L^{-1}).

Effect of temperature and adsorbent dose

The combined effect of temperature and adsorbent dose on dye uptake is shown in Fig. 4c. It may be noted that the dye sorption increase with both the temperature and adsorbent dose. The observed trend may be understood that the increase in dose would make higher number of adsorption sites available, resulting into higher adsorption rate. A maximum dye removal (>496 mg g^{-1}) was observed at constant pH (6.9) and dye concentration (200 mg L^{-1}).

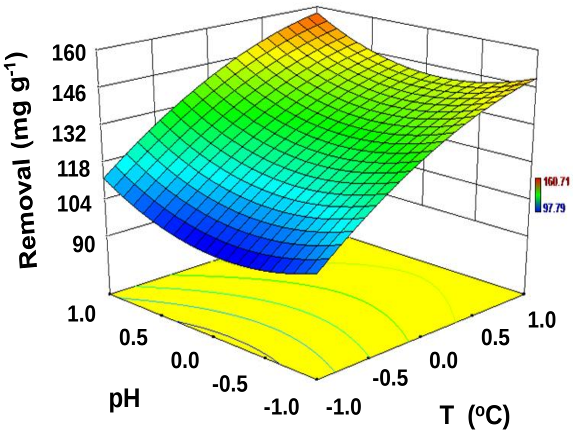


Figure 4 (a): Temperature and pH

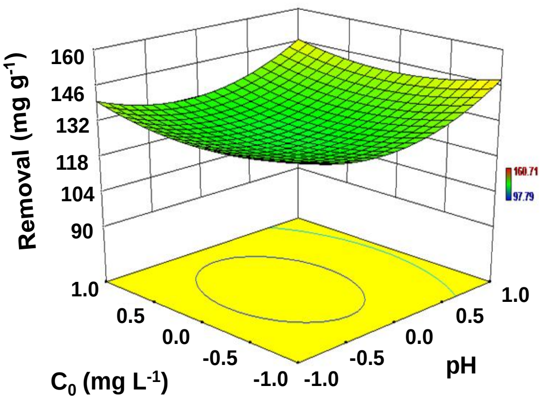


Figure 5(a): pH and initial dye concentration

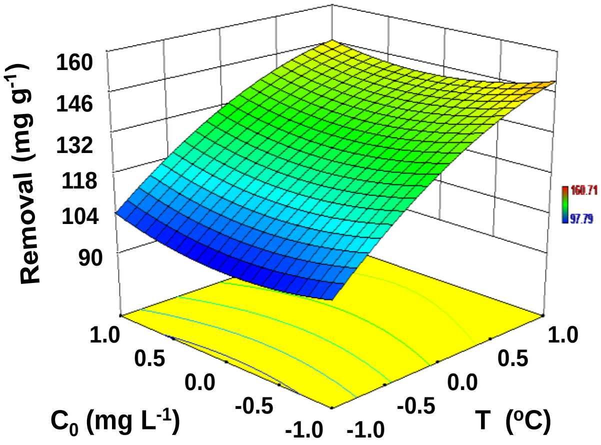


Figure 4 (b): Temperature and initial dye concentration

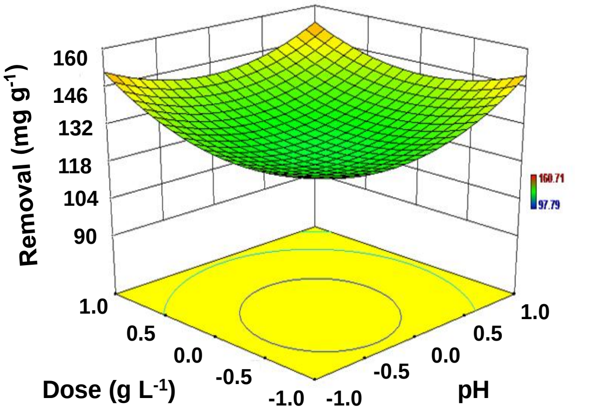


Figure 5 (b): pH and adsorbent dose

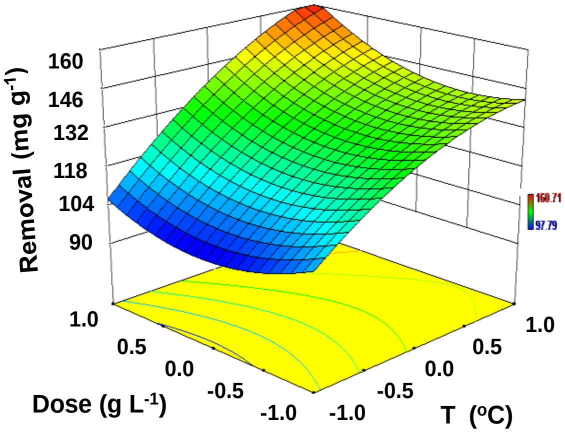


Figure 4 (c): Temperature and adsorbent dose

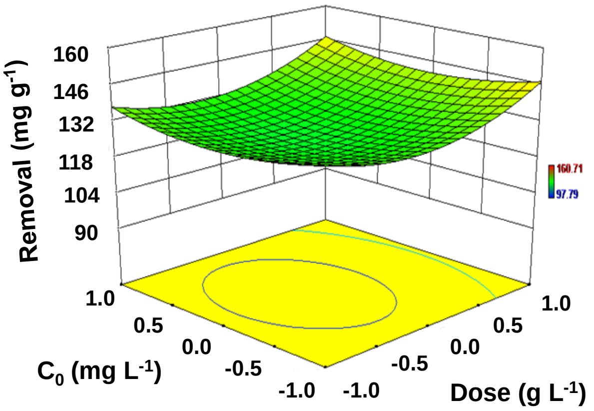


Figure 5 (c): Adsorbent dose and initial dye concentration

Effect of pH and initial dye concentration

The interactive effect of pH and initial dye concentration on adsorption from the aqueous phase is shown in Fig. 5a. It is evident that the dye uptake increase with increasing pH of the solution and declines with increase in the dye concentration in the experimental range as in cases discussed earlier. A maximum dye removal (>156 mg g^{-1}) was observed at constant temperature (30°C) and adsorbent dose (0.4 g L^{-1}).

Effect of pH and adsorbent dose

Figure 5b shows the interactive influence of solution pH and adsorbent dose on dye uptake. It suggests that dye uptake increase with both the increase in solution pH and adsorbent dose. Such a pattern of dye sorption may be explained in terms of the solution pH and pH_{ZPC} of the CCAC, which attains reversal of charge density below and above its zero point charge pH. A maximum dye uptake is observed at pH 9 and adsorbent dose of 2.5 g L^{-1}. A maximum dye removal (> 496 mg g^{-1}) was observed at constant temperature (30°C) and initial dye concentration (200 mg L^{-1}).

Effect of initial dye concentration and adsorbent dose

The combined effect of adsorbent dose and dye concentration on dye uptake by the adsorbent is visible in Fig. 5c. It may be seen that increasing dose level results in an increasing adsorption of the dye, whereas, it decreases with the dye concentration. An optimum dye uptake is observed at the highest adsorbent dose and the lowest dye concentration. At constant temperature (30°C) and dose (2.5 g L^{-1}), a maximum dye removal (>496 mg g^{-1}) was determined.

Response optimization and confirmation experiment

The main goal of the optimization process is that to determine the optimum values of independent variables for maximum dye removal using CCAC. The developed mathematical model was optimized using quadratic programming to get maximum efficiency of CCAC for dye removal. The numerical optimization suggested the optimum values of different process variables (viz. temperature 49.9°C, pH 8.94, initial dye concentration 153.91 mg L^{-1}, and adsorbent dose 0.4 g L^{-1}) to achieve the maximum removal (166.6 mg g^{-1}) of the MB dye from the solution in an equilibrium time of 1.5 h. this results was validated experimentally (166.7 mg g^{-1}, removal), which is very close to the optimum value predicted by the model at optimum condition.

Comparison of various adsorbents

The removal of MB by different adsorbents has been studied extensively, and dye adsorption capacities were reported in literatures. Table 7 compares the adsorption capacities of the CCAC obtained in this work with different adsorbents previously used for removal of dyes. It can be seen from Table 7 that the adsorption capacities of the prepared CCAC for MB dye are much higher than that of many other previously reported adsorbents, indicating that the CCAC is a better adsorbent for their application in MB dye removal from aqueous solution.

Table 7: Comparison of the maximum adsorption capacity of MB from various adsorbents

Adsorbents	Adsorption capacity (mg g^{-1})	References
Coir pith	120.43	[34]
Diatomite	156.6	[35]
Garlic peel	82.64	[36]
Wood apple shell	95.2	[37]
MMT/ $CoFe_2O_4$ composite	97.75	[38]
Carbon nano tube	48.06	[39]
Palm kernel fiber	95.4	[40]
Agar	50	[41]
Corn cob activated carbon	160.71	This work

Desorption of MB dye

Desorption of the MB dye adsorbed on the CCAC was performed using the 0.1 M NaOH and HCl. Desorption studies help to elucidate the mechanism of adsorption and recovery of the adsorbate and adsorbent. About 1.78% of the sorbed MB dye mass was recovered by the NaOH solution and about 38% of the sorbed MB dye mass was recovered by the HCl solution.

Conclusion

A Box-Behnken Design was conducted to investigate the influence of key factor such as temperature, solution pH, initial dye concentration and adsorbent dose on the MB dye removal process by CCAC with the response surface methodology. Analysis of variance showed a high coefficient of determination value (R^2= 0.98) ensuring a satisfactory adjustment of the second order polynomial regression model with the experimental data. Process optimization was carried out, under the optimal conditions of independent variables, the maximum MB dye removal capacity of CCAC was found 166.6 mg g^{-1}, which is very close to the experimentally determined value (166.7 mg g^{-1}). It is concluded that temperature & adsorbent dose produced the largest effect on adsorptive removal of MB dye from aqueous medium by CCAC and CCAC can be used as potential adsorbent for removal of MB dye from water contaminated with MB dye under optimized conditions.

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