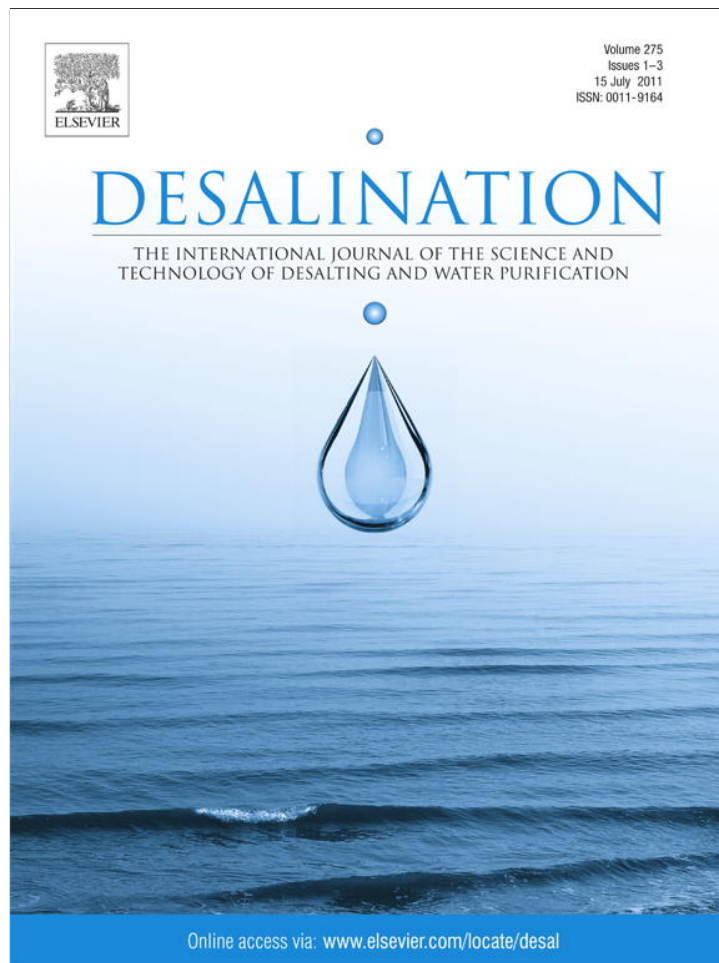


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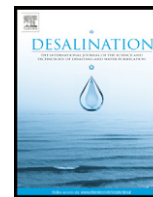
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# Application of Response Surface Methodology for preparation of low-cost adsorbent from citrus fruit peel and for removal of Methylene Blue

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## ABSTRACT

A low-cost adsorbent has been prepared by carbonizing citrus fruit peel using o-phosphoric acid as an activating agent and investigation has been made to explore the possibility of this adsorbent for liquid phase adsorptive removal of Methylene Blue (MB), selected as a model dye. Operating parameters for carbonization of citrus fruit peel viz., weight ratio of citrus fruit peel to activating agent, temperature and time of carbonization have been optimized by Response Surface Methodology (RSM) considering decolorizing power of prepared sample as response. The carbonized sample prepared at optimum condition as designated by Design Expert Software is termed as Charred Citrus Fruit Peel (CCFP). Physico-chemical characterization of CCFP is done and the study reveals that BET surface area of CCFP is 526 m<sup>2</sup>/g, which is very much comparable to that of commercial activated carbon. Detailed kinetic and equilibrium studies have been performed for liquid phase adsorption of MB using CCFP. Response Surface Methodology has also been applied to model statistically the adsorptive removal of MB from its aqueous solution in batch process using CCFP and to optimize process variables. Maximum 99.08% removal was achieved during kinetic study in a batch contactor.

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## 1. Introduction

Textile industry is becoming one of the largest growing industries in India. The waste water coming from textile industries contain considerable amount of dyes which may cause severe environmental pollution if they are emitted to the environment without any proper treatment [1–23]. Among various dyes, MB is the most frequently used substance for dyeing silk, wood and cotton [10]. It has severe impact on human health such as ingestion through mouth may cause nausea, vomiting, diarrhea etc. [10–21]. Thus, removal of MB from waste water is of great concern from environmental point of view. Among the various methods for dye removal like, flocculation, precipitation, ion exchange, electro-kinetic coagulation, ozonation, etc., the adsorption process is one of the most efficient methods due to its simplicity of design, ease of operation and insensitivity to toxic substances [6]. Although commercial activated carbon is the preferred adsorbent for dye removal because of its extended surface area, microporous structure and high adsorption capacity, its widespread use is restricted due to its high capital and regeneration cost [2,3,24]. Thus, researches are now tending towards the development of new low-cost adsorbent from various non-conventional waste materials from industries and agriculture, having equivalent potential as that of

commercial activated carbon. Though a number of studies have been made in this line [1–7,21–27], no investigation was made to explore the possibility of usage of citrus fruit (grape fruit) peel, a market waste, as the precursor for activated carbon preparation. Thus, in the present work, an attempt has been made to prepare a low-cost adsorbent from citrus fruit peel by carbonizing it through chemical activation method. Citrus fruit peel has no use after the extraction of juice from the fruit and is thus inexpensive and readily available and being a market waste, citrus fruit peel causes disposal problem vis-à-vis environmental pollution. Thus, conversion of citrus fruit peel to low-cost adsorbent serves double purposes. Firstly, unwanted market waste is converted to value added product and secondly, this product may be efficiently used for abatement of environmental pollution.

An adsorbent is characterized by its adsorption capability which is very much dependent on the preparation condition. As carbonization through chemical activation method is used in the present study for preparation of adsorbent from citrus fruit peel, weight ratio of peel to activating agent, temperature and time of carbonization are selected as process variables and optimization of these process variables is very much essential from efficient adsorbent preparation point of view. Usually process variables are optimized by studying the response at constant values of independent variables. The limitations associated with this conventional method are non-depiction of combined effect of all the independent variables at a single time, greater time consumptions due to more number of experiments and non-reliability of results [7,8]. These shortcomings can be eliminated by optimizing all the affecting process variables collectively by

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statistical experimental design such as RSM [7–10,26–29]. Though optimization through RSM is quite common in various processes, only very few investigators [30–33] have used it for finding out optimum condition of carbonization for preparation of adsorbent. Thus, in the present study, RSM is used to determine the optimum carbonization condition for preparation of low-cost adsorbent from citrus fruit peel and to assess the interactive effect of the process variables on the response. The adsorbent prepared from citrus fruit peel at the optimum condition is termed as Charred Citrus Fruit Peel (CCFP) and used for further studies on MB removal.

To assess the mechanism of adsorption process and to evaluate the kinetic parameters useful for designing of continuous adsorber, a detailed kinetic study has been performed by varying three operating parameters viz., initial concentration of MB, the amount of CCFP and size of CCFP in a prescribed manner. Equilibrium study has also been carried out to determine maximum adsorption capacity of CCFP. In another study, RSM is used to optimize process variables for removal of MB by CCFP and to assess interactive effects between them. Thus, in the present paper, RSM is used both for optimization of carbonization condition as well as for optimization of process variables for MB removal using CCFP, a low-cost novel adsorbent.

## 2. Materials and methods

### 2.1. Optimization of carbonization condition of citrus fruit peel and preparation of Charred Citrus Fruit Peel (CCFP)

#### 2.1.1. Experimental

Citrus fruit (grapefruit) peel was collected from a local juice maker and washed thoroughly with distilled water to remove any acidic substances and dirt. It was then dried in sunlight for 2 days. Dried citrus fruit peel was fed to a mixer and grinder and thus ground. Then any one of the following activating agent like, ortho-phosphoric acid (88% GR, MERCK) or zinc chloride (MERCK) or sulfuric acid (98% Pure, MERCK) was mixed with the dried powdered fruit peel of size lesser than 90  $\mu\text{m}$ . This was then carbonized in a muffle furnace by heating it at an elevated temperature. The weight ratio of dried citrus fruit peel to activating agent was varied in the range of 1:1 to 3:1, temperature in the range of 450°C–550°C and the time of carbonization was varied from 0.75 h to 1.5 h. The charred material was cooled and washed with dilute ammonia solution (A.R. Grade, SARA Fine Chemicals Pvt. Limited) and then with distilled water in order to remove any unconverted activating agent from carbonaceous material. The washing of the sample was continued until the pH of the filtrate was found to be exactly 7. The charred material was left for drying overnight in ambient conditions. The dried samples were crushed and fractionated into different size fractions. The decolorizing power (mg MB removed/g charred sample) for each sample was tested using particle of size lesser than 90  $\mu\text{m}$  following standard procedure [24]. Methylene Blue (AR grade, MERCK) was used. Optimization work has been done by RSM using Design Expert Software. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions [7,8,27]. The main objective of RSM is to determine the optimum operational conditions of the system or to determine a region that satisfies the operating principles [34,35]. It usually contains three stages: (i) design and experiments, (ii) response surface modeling through regression, and (iii) optimization [36]. Initially four parameters such as activating agents, weight ratio of citrus fruit peel to activating agent, temperature and time of carbonization had been selected to be optimized for preparation of adsorbent. Design Expert Software was used for such purpose. Initially three activating agents viz., zinc chloride, sulfuric acid and ortho-phosphoric acid had been considered to be used for carbonization of citrus fruit peel. Type of activating agent had been considered as one

categoric factor whereas other parameters like, weight ratio of peel to activating agent, temperature and time of carbonization, had been considered as numeric factors according to the software. To reduce the number of experimental runs, the number of categoric factors had been restricted to zero by selecting the best activating agent. This was done by examining the decolorizing power of charred sample (mg MB removed/g charred sample) prepared by carbonizing citrus fruit peel using each activating agent separately. Results showed that ortho-phosphoric acid was the best activating agent among others and it was selected for operation. Finally, experiments had been designed statistically by varying three numeric factors viz., weight ratio of citrus fruit peel to activating agent (1.0–3.0), temperature of carbonization (450 °C–550 °C), and time (0.75–1.5 h) suitably.

#### 2.1.2. Design of experiments

The parameters for preparation of adsorbent were optimized by RSM. Principally, this optimization process follows three major steps consisting of carrying out statistically designed experiments, evaluating the coefficients in a mathematical model with prediction of response and examining the adequacy of the model [27]. One significant contribution in this field is done by Singh et al. [37]. RSM helps to quantify the relationships between one or more measured responses and the vital input factors.

$$Y = f(X_1, X_2, \dots, X_n) \quad (1)$$

where, Y is the response of the system and  $X_i$ s are the independent variables called factors [27].

For three independent variables, the total numbers of tests required is

$$N = 2^n + 2n + n_c = 2^3 + 2 \times 3 + 6 = 20 \quad (2)$$

as shown by Sahu et al., 2009 [27].

The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors [8,27]. The result of each run was analyzed and the response was correlated with three independent parameters for preparation of adsorbent by carbonization using an empirical second degree polynomial equation such as

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \left( \sum_{i=1}^n \beta_{ii} X_i \right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} X_i X_j \quad (3)$$

where,  $\beta_0$  is the constant coefficient,  $\beta_i$  is the linear coefficient,  $\beta_{ii}$  is the quadratic coefficients,  $\beta_{ij}$  is the interaction coefficients [7,8,26,27].

The independent parameters and the dependent output response were modeled and optimized using ANOVA to estimate the statistical parameters. The maximum (+1) and minimum level (−1) of three numeric factors viz., weight ratio of citrus fruit peel to activating agent, temperature of carbonization and time of carbonization were 1:1 and 3:1 (i.e., 1 and 3), 450 °C and 550 °C and 0.75 h and 1.5 h respectively. The experimental design as suggested by Design Expert Software along with the values of responses is presented in Table 1. According to the software, the optimized condition for carbonization of citrus fruit peel is obtained when weight ratio of peel to activating agent, temperature of carbonization and time of carbonization have the values of 3:1, 524.86 °C and 0.75 h respectively. The adsorbent thus obtained is termed as Charred Citrus Fruit Peel (CCFP). Further studies on dye removal were carried out with CCFP.

#### 2.2. Characterization of CCFP

The physico-chemical characterization of CCFP was determined following standard procedure [24]. The properties estimated include bulk density, solid density, moisture content, ash content, etc. To keep the mass transfer resistance negligibly small, the particles having the

**Table 1**  
Experimental design for preparation of CCFP.

Run	Weight Ratio (A, g/g)	Temperature (B, °C)	Time (C, h)	Decolorizing power (R <sub>1</sub> , mg/g)
1	2	415.91	1.13	9.7087
2	2	584.09	1.13	10
3	2	500	0.49	8.5258
4	2	500	1.13	6.8945
5	2	500	1.13	6.8945
6	1	450	0.75	10.2688
7	3	450	0.75	7.2659
8	2	500	1.13	6.8945
9	3.68	500	1.13	10.508
10	2	500	1.13	6.8945
11	2	500	1.13	6.8945
12	3	550	0.75	9.4216
13	1	450	1.50	15.847
14	3	450	1.50	10.3808
15	1	550	0.75	9.15217
16	3	550	1.50	9.3558
17	2	500	1.13	6.8945
18	2	500	1.76	11.3944
19	1	550	1.50	11.2484
20	0.32	500	1.13	13.078

size below 90 μm is used during determination of these properties. To compare CCFP with commercial activated carbon (MERCK), same tests were performed with the later one using the same protocol.

### 2.2.1. Scanning Electron Microscopy (SEM)

SEM studies of CCFP, commercial activated carbon (MERCK) and CCFP after adsorbing MB were performed to obtain their topographical characterization. The samples were mounted on brass stubs using double-sided adhesive tape. SEM photographs were taken with scanning electron microscope (HITACHI S-3000N, JAPAN) at the required magnification at room temperature. The working distance of 25 mm was maintained and acceleration voltage used was 15 kV, with the secondary electron image (SEI) as a detector.

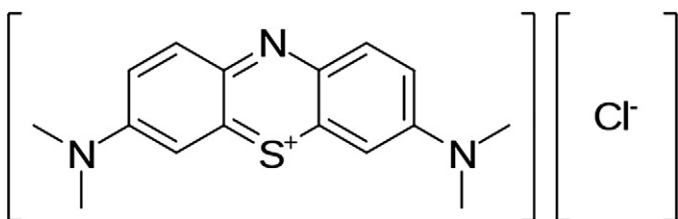
### 2.2.2. Analyses of BET surface area and pore volume of CCFP

Surface area of CCFP was measured by BET method. Measuring instrument used was Quantachrome make NOVA 4000e (USA). CCFP was also tested for Pore Size Distribution and Pore Volume using Mercury Intrusion Method. Measuring instrument used was Quantachrome make Poremaster 60 (USA). To compare these properties with commercial activated carbon, same tests were performed with commercial activated carbon (MERCK).

## 2.3. Removal of MB using CCFP

### 2.3.1. Kinetic study

To establish the mechanism of dye removal using CCFP, kinetic study was done. A stock solution of MB was prepared by dissolving definite amount of MB (AR grade, MERCK) in distilled water. The chemical structure of Methylene Blue is shown below.



The general properties of MB are as follows: (i) Appearance: Dark green crystals with bronze luster or crystalline powder; (ii) Odor: Odorless; (iii) Solubility: Soluble in water; (iv) Boiling point: Decomposes; (v) Melting point: 100–110°C. Various concentrations of MB solution were prepared from the stock solution by diluting it with suitable amount of distilled water. The dye solution was contacted with specific amount of CCFP in a batch contactor. To eliminate the mass transfer resistance and to make the process adsorption rate controlled, the solution was stirred continuously. The liquid samples were taken at a particular interval and filtered under vacuum to get rid of adsorbent and analyzed. The process parameters like initial concentration of dye (25–100 mg/L), weight of adsorbent (0.25 g–1 g) and size of adsorbent (135–275 μm) were varied in a prescribed manner. The concentration of residual MB in solution was analyzed spectrophotometrically using UV–Visible Spectrophotometer (UV 2300, TECHCOM, GERMANY) at 660 nm.

### 2.3.2. Equilibrium study

For equilibrium study 100 ml stock MB solution was prepared and diluted to obtain desired concentration of MB solution (10 ppm–100 ppm). 0.75 g of CCFP was added to each flask and the lid was closed and they were placed overnight in a BOD incubator with shaker. Equilibrium studies were performed at two different temperatures viz., 20°C and 35°C respectively. Finally the solutions were centrifuged and the clear liquid was analyzed spectrophotometrically at 660 nm.

### 2.3.3. Optimization of MB removal using CCFP by RSM

**2.3.3.1. Experimental.** From kinetic study of MB removal using CCFP in a batch contactor it is seen that the size of CCFP has negligible effect on the removal of MB under the ranges studied. Therefore, during optimization using RSM, this parameter has not been considered whereas, three other process parameters viz., initial concentration of MB, amount of adsorbent and pH of solution were considered as numeric factors and percentage removal of MB was considered as response. Major removal has been achieved within 10 min. Kinetic study also reveals that percentage removal of MB reaches to its saturation value at about 60 min. Thus, during the study for optimization of process variables of MB removal, time of operation has been fixed at 8 h. 200 ml of MB solution having specific concentration was contacted with specified amount of CCFP in a batch contactor for 8 h. The concentration of solution, pH of solution and amount of adsorbent were maintained according to the statistical design as specified by the software. The concentration of residual MB in solution was analyzed spectrophotometrically.

**2.3.3.2. Design of experiments.** As discussed in the Sec. 2.1.2, RSM can be used for optimization of process variables. In the present study, optimum condition for MB removal using CCFP by the application of RSM was determined. The maximum (+1) and minimum level (−1) of three numeric factors viz., initial concentration of MB, weight of CCFP and pH were, 10 mg/l and 30 mg/l, 0.30 g and 1.0 g and 5 and 9 respectively. The experimental design as suggested by Design Expert Software along with the values of responses is presented in Table 2.

## 3. Results and discussions

### 3.1. Optimization of carbonization condition of citrus fruit peel and preparation of Charred Citrus Fruit Peel (CCFP)

Three parameters viz., weight ratio of peel to activating agent, temperature and time of carbonization have been optimized by RSM using Design Expert Software for carbonization of citrus fruit peel. The list of experiments as designed by RSM and the values of response (decolorizing power) for each sample obtained at corresponding

**Table 2**  
Experimental design for removal of MB.

Run	Weight of CCFP (A', g)	pH (B')	Initial concentration of MB (C', mg/l)	Percentage removal of MB (R <sub>2</sub> , %)
1	1.24	7	20	99.80
2	0.06	7	20	95.002
3	0.30	5	30	98.10
4	0.65	10.36	20	97.50
5	0.65	7	20	99.50
6	0.30	9	30	94.00
7	0.65	7	20	99.50
8	0.65	7	36.82	97.50
9	0.65	7	20	99.5
10	1	5	30	99.01
11	0.65	7	20	99.50
12	0.65	7	20	99.50
13	1	5	10	99.0941
14	0.65	3.64	20	99.6225
15	0.30	5	10	99.00
16	0.65	7	3.18	99.90
17	0.30	9	10	98.002
18	1	9	10	99.7484
19	1	9	30	98.79
20	0.65	7	20	99.5

experimental conditions are shown in Table 1. The regression analysis was performed to fit the response. As suggested by the software, no transformation was chosen and quadratic process order was selected to analyze data. The final regression function for response in terms of coded factors used in making of statistical model is given below:

$$R_1 = + 6.91 - 1.06 \times A - 0.30 \times B + 1.14 \times C + 0.86 \times A \times B - 0.58 \times A \times C - 0.83 \times B \times C + 1.65 \times A^2 + 0.96 \times B^2 + 1.0 \times C^2 \quad (4)$$

where  $R_1$  = decolorizing power (mg MB removed/g charred sample),  $A$  = Weight ratio (g/g),  $B$  = temperature of carbonization ( $^{\circ}\text{C}$ ),  $C$  = time of carbonization (h).

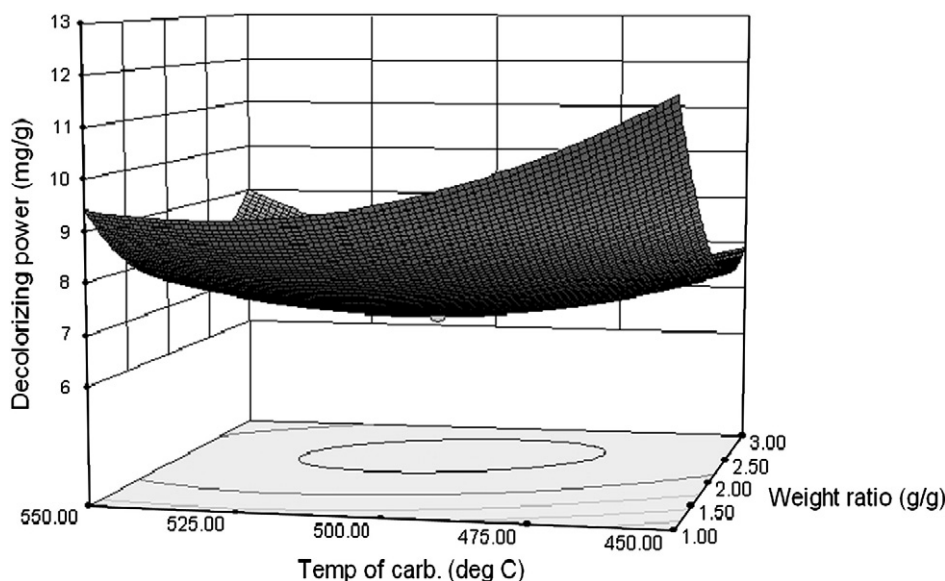
Based on the analysis done by ANOVA, it has been found that weight ratio and time of carbonization have significant effect on decolorizing power. On the other hand quadratic effects of weight ratio, temperature of carbonization and time of carbonization have significant effect on decolorizing power. The interaction effects of weight ratio and temperature of carbonization, weight ratio and time

of carbonization and temperature and time have been found to be significant.

Fig. 1 shows the three dimensional response surface of the combined effect of temperature and weight ratio on decolorizing power at constant time of carbonization ( $C = 1.125$  h). Figure reveals that samples prepared at  $450^{\circ}\text{C}$  with weight ratio 1.0 shows the maximum decolorizing power. From the figure it is also evident that with increase in weight ratio, decolorizing power is decreasing up to a certain point then increasing a little at constant temperature. This is also true in the case of temperature variation. With increase in temperature, decolorizing power is decreasing up to a certain temperature and then increasing at constant weight ratio. The maximum decolorizing power has been obtained when temperature and weight ratio both are minimum and again when temperature and weight ratio have maximum values. This may be due to the synergic effect of temperature of carbonization and amount of activating agent on decolorizing power of prepared samples. Large weight ratio means less amount of activating agent and thus higher temperature is required to get higher decolorizing power. On the other hand, lower temperature is sufficient when amount of activating agent is more and this is true when weight ratio is small.

Fig. 2 represents the conjugate effect of time and weight ratio at constant temperature of carbonization ( $B = 500^{\circ}\text{C}$ ). Figure shows that carbonization for 1.5 h with weight ratio 1.0 gives the maximum decolorizing power. Decolorizing power decreases with increase in weight ratio up to a certain point then it increases with increase in weight ratio and it is also evident from the figure that decolorizing power increases with increase in time of carbonization. Maximum decolorizing power obtained at lower values of weight ratio and higher time. This phenomenon can be attributed to the synergic effect of time and amount of activating agent. As stated earlier, higher weight ratio denotes lesser amount of activating agent and thus, more time is required to get proper carbonization. Similar observation is obtained when the conjugate effect of time and temperature is shown in Fig. 3. The figure reveals that carbonization at  $450^{\circ}\text{C}$  for 1.5 h produces the sample having maximum decolorizing power and carbonization for 0.75 h at  $450^{\circ}\text{C}$  provides the sample having minimum decolorizing power. This is very obvious due to the fact that at lower time and temperature, carbonization process would not be completed.

The actual and predicted responses are shown in Fig. 4. Actual values are experimentally measured response data for a particular run



**Fig. 1.** Combined effect of temperature of carbonization and weight ratio on decolorizing power for preparation of CCFP.

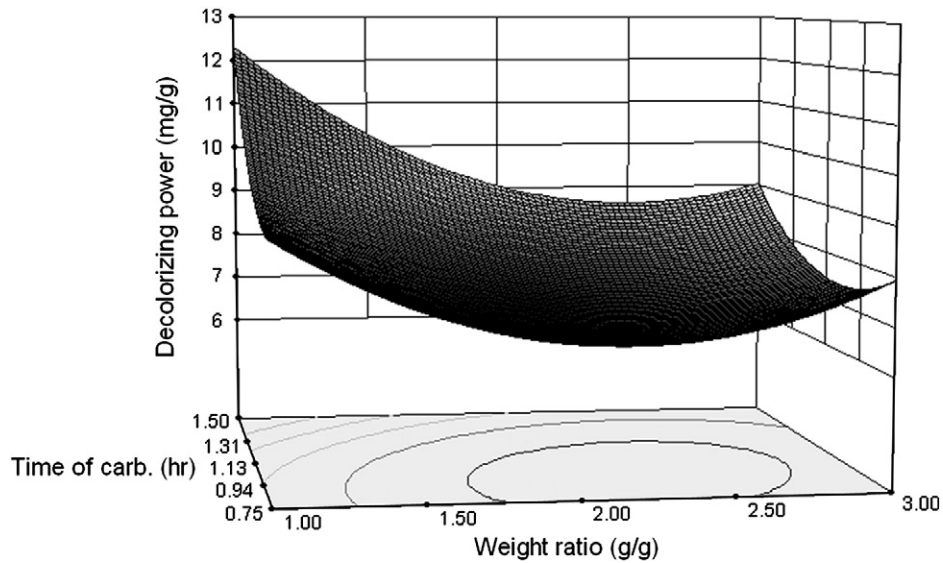


Fig. 2. Combined effect of time of carbonization and weight ratio on decolorizing power for preparation of CCFP.

and the predicted values are evaluated from the model and that is generated by using the prediction equation. The statistical parameters obtained are shown in Table 3. The fair values of statistical parameters are due to the selection of different variables in wide ranges with a limited number of experiments. It is well-known that carbonization temperature has pronounced effects on the quality of charred sample. Very low temperature is insufficient for proper carbonization and very high temperature may destroy the surface properties of the adsorbent leading to lower values of decolorizing power of the sample [24]. Again higher temperature of carbonization, lower weight ratio and higher time of carbonization incur cost to the process. Thus, during optimization of carbonization condition, constraints related to these parameters are chosen in such way that carbonization cost should be low.

According to the Design Expert Software, the optimized condition is obtained when weight ratio of peel to activating agent, temperature and time of carbonization have the values of 3, 524.86°C and 0.75 h respectively. The carbonized sample obtained at this condition has been termed as Charred Citrus Fruit Peel (CCFP) and used for further studies on MB removal.

### 3.2. Characterization of CCFP

CCFP has been characterized in terms of solid density, bulk density, moisture content, ash content, BET surface area, pore volume. Data are shown in Table 4. To compare CCFP with commercial activated carbon, the properties of activated carbon have also been listed in Table 4. From the table it is evident that these two adsorbents are quite similar in their properties. Density is very important property in removal process. If two carbon samples having different bulk density are taken in same amount per unit volume of adsorber, the carbon sample having greater bulk density will adsorb more amount of adsorbate [27]. The bulk density and solid density of CCFP have been found to be 2008 kg/m<sup>3</sup> and 1234 kg/m<sup>3</sup>. High values indicate good carbonization of citrus fruit peel. Ash content of the adsorbent has been determined by taking the weight of residue left in the crucible after burning the adsorbent in a specific manner. Ash content of the adsorbent is generally considered as impurity and has no use in adsorption process [27]. Thus, low ash content resembles CCFP as a good adsorbent. Again, being a surface phenomenon, adsorption process is directly proportional to available surface area of adsorbent. In the present

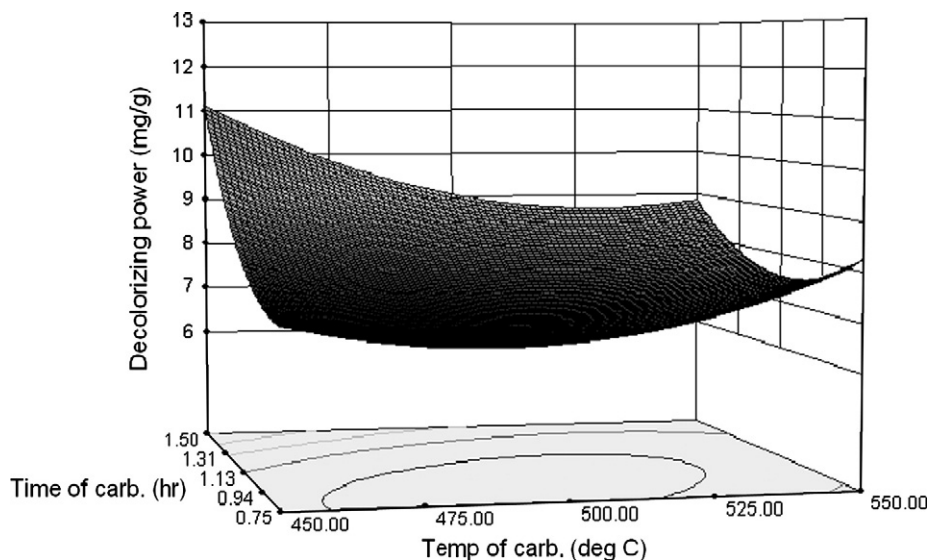


Fig. 3. Combined effect of time of carbonization and temperature of carbonization on decolorizing power for preparation of CCFP.

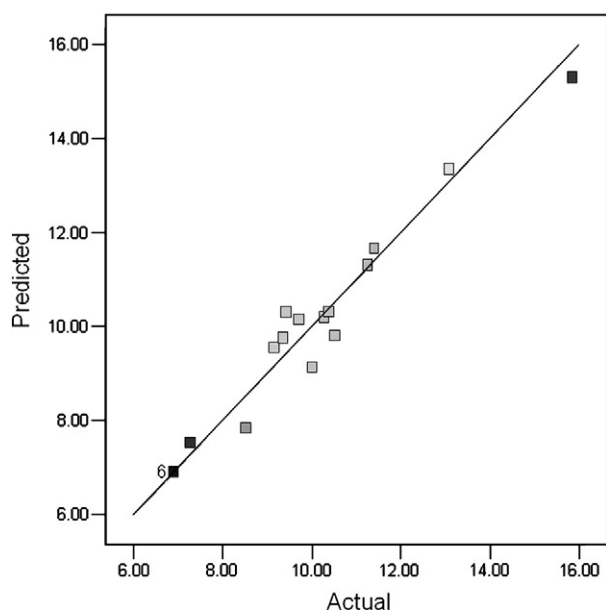


Fig. 4. Plot of actual response versus predicted response for preparation of CCFP.

**Table 3**  
Values of statistical parameter.

Statistical parameter	Values
R-squared	0.9675
Adj R-squared	0.9382
Pred R-squared	0.7528

study, high value of BET surface area (526 m<sup>2</sup>/g) indicates good adsorptive property of CCFP.

### 3.2.1. Scanning electron microscopy (SEM)

Fig. 5a, b and c show the scanning electron microscope (SEM) image of CCFP, commercial activated carbon and CCFP after adsorption of MB. Fig. 5a demonstrates the porous structure of CCFP. The photograph is very much similar to that of commercial activated carbon (Fig. 5b). A polishing/smoothing effect has been observed in Fig. 5c which is absent in Fig. 5a. This may be due to the fact that adsorption of MB molecule over CCFP makes the surface of CCFP smoother than its original form.

### 3.3. Removal of MB using CCFP

#### 3.3.1. Kinetic study

To establish the mechanism of adsorption process and to determine kinetic parameters useful for designing of continuous adsorber, a detailed kinetic study has been performed by varying three operating

**Table 4**  
Characterization of CCFP and commercial activated carbon (MERCK).

Properties	CCFP	Activated carbon
Bulk density (kg/m <sup>3</sup> )	2008	2600
Solid density (kg/m <sup>3</sup> )	1234	988.43
Moisture content (%)	17.36	12.81
Ash content (%)	10.92	7.13
BET surface area (m <sup>2</sup> /g)	526	750
Pore volume (cc/gm)	1.3864	0.8956

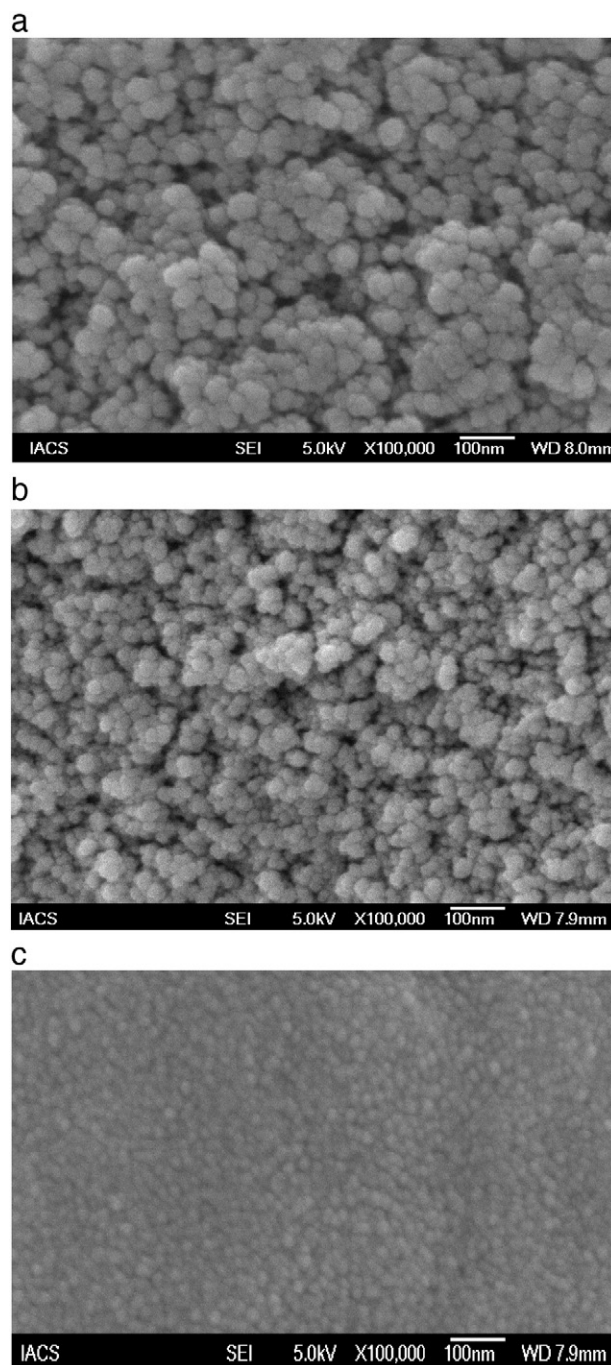
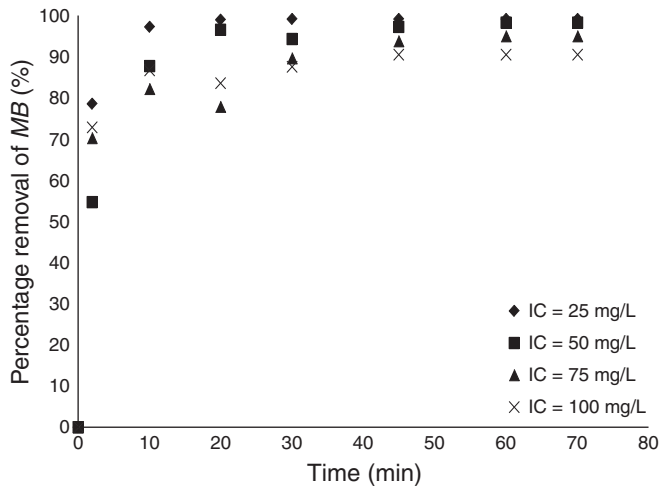


Fig. 5. a. Scanning electron micrograph of CCFP. b. Scanning electron micrograph of commercial activated carbon (MERCK). c. Scanning electron micrograph of CCFP after adsorption of MB.

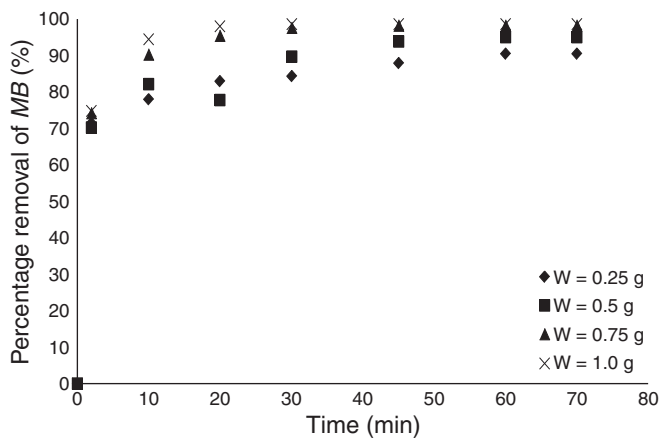
parameters viz., initial concentration of MB (25–100 mg/L), the amount of CCFP (0.25–1.0 g) and size of CCFP (135–275 μm) in a prescribed manner. Kinetics of adsorption has been determined by analyzing the adsorptive uptake of the MB from aqueous solution at different time intervals. The result reveals that MB can be removed maximum about 99.08% from its aqueous solution using CCFP at pH 7, when initial dye concentration and weight of CCFP were 25.0 mg/L and 0.75 g respectively. Fig. 6 represents the percent removal–time histories for MB when initial concentration of dye varies from 25 mg/L to 100 mg/L keeping all other parameters viz. weight of CCFP, size of CCFP, pH and temperature constant at 0.75 g, 135 μm, 7



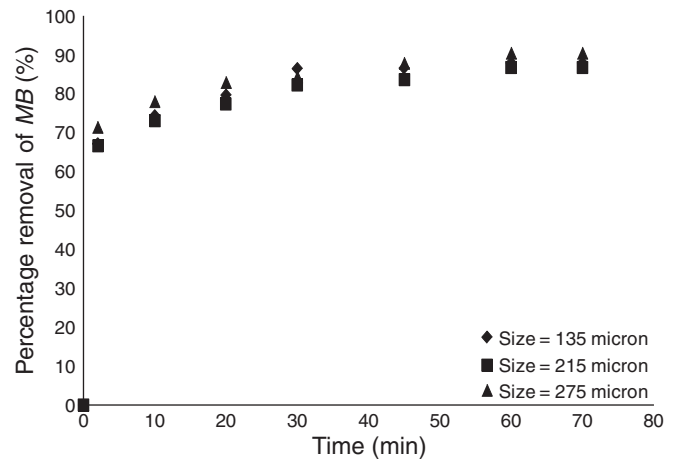
**Fig. 6.** Time histories of percentage removal of MB with initial concentration of MB as parameters. In all cases weight of CCFP, particle size of CCFP, pH and temperature are fixed at 0.5 g, 135  $\mu\text{m}$ , 7 and 30  $^{\circ}\text{C}$  respectively.

and 30  $^{\circ}\text{C}$  respectively. From the figure it is evident that initially the rate of disappearance of the adsorbate is high for the solution with lower initial concentration but after 60 min of operation, the curves become nearly parallel to each other indicating that the rate of disappearance of adsorbate is nearly identical. It is also evident that the adsorption process has two regimes. In the first regime, the process is fast as dye molecules in solution can interact with surface of CCFP readily. In the second regime the rate of adsorption is decelerating and reaching to equilibrium values. Similar observation has been made by Asheh et al. [38]. It is also evident from Fig. 6 that maximum removal has been achieved within 60 min and after that no removal is observed. This indicates that equilibrium is reached within these 60 min of operation.

To examine the effect of amount of CCFP on the percentage removal of dye, the later has been plotted against time in Fig. 7 by varying the amount of CCFP ( $W$ ) in the range of 0.25–1.0 g. For all the cases initial concentration of dye, size of CCFP, pH and temperature are kept constant at 75 mg/L, 135  $\mu\text{m}$ , 7 and 30  $^{\circ}\text{C}$  respectively. The figure reveals that MB has been removed from 90.53% to 98.55% with increase in amount of CCFP from 0.25 to 1.0 g. Similar to the previous cases; major portions of dye are removed within first 10 min.



**Fig. 7.** Time histories of percentage removal of MB with weight of CCFP as parameters. In all cases initial concentration of MB, particle size of CCFP, pH and temperature are fixed at 75 mg/L, 135  $\mu\text{m}$ , 7 and 30  $^{\circ}\text{C}$  respectively.



**Fig. 8.** Time histories of percentage removal of MB with particle size of CCFP as parameters. In all cases initial concentration of MB, weight of CCFP, pH and temperature are fixed at 75 mg/L, 0.5 g, 7 and 30  $^{\circ}\text{C}$  respectively.

In Fig. 8, the percentage removal of MB, obtained experimentally by varying the particle size of CCFP in the range of 135–275  $\mu\text{m}$ , has been plotted against time keeping other parameters like initial concentration of dye, weight of CCFP, pH and temperature constant at 75 mg/L, 0.75 g, 7 and 30  $^{\circ}\text{C}$  respectively. It is evident from the figure that the percentage removal of dye is almost same (87.98%–90.53%) in all the cases irrespective of the particle size. This may be attributed to the negligible mass transfer resistance of CCFP in the range of particle sizes studied. Thus, during optimization study of MB removal, particle size has been kept constant at 135  $\mu\text{m}$  and is not considered as a parameter.

Three kinetic models viz., Morris–Weber model, the Lagergren model and the Pseudo Second Order model (PSOM) have been used to analyze the data obtained during kinetic study in a batch contactor. Morris–Weber model assumes that if intraparticle diffusion is involved in the sorption process, then a plot of the square root of time versus the uptake would result in a linear relationship [38,39]. If this line passes through the origin, then intraparticle diffusion would be the rate-controlling step of the sorption process [38,39]. The equation for Morris–Weber model is as follows

$$q_t = k_M t^{1/2} \quad (5)$$

Lagergren first-order kinetic model proposes a first-order kinetic rate based on surface reaction [38,39]. This model can be described by the following equation.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

Pseudo Second Order model (PSOM) assumes that the sorption process is of pseudo-second-order and that the rate-limiting step is of chemisorption nature [38,39]. The mechanism may involve valence forces by sharing or through the exchange of electrons between sorbent and sorbate. The equation for PSOM is

$$\frac{t}{q_t} = \frac{1}{k_p q_e^2} + \frac{t}{q_e} \quad (7)$$

Among these three models, PSOM fits more accurately with the kinetic data obtained for various initial concentration of MB (25–100 mg/L), size (135–275  $\mu\text{m}$ ) and amount of adsorbent (0.25–1.0 g) as shown in Figs. 6–8. Results imply that the adsorption process is of



**Table 5**  
Values of kinetic parameters.

Model equation	Parameters varied		
	Initial concentration of Methylene Blue	Weight of adsorbent	Size of adsorbent
Moris Weber model $q_t = k_M t^{1/2}$	$k_M = 3.9075$ $R^2 = 0.310$	$k_M = 4.7667$ $R^2 = 0.279$	$k_M = 4.343$ $R^2 = 0.2954$
Lagergren model $\log(q_e - q_t) = \log q_e - \frac{k_L t}{2.303}$	$k_L = 0.0389$ $R^2 = 0.4595$	$k_L = 0.0454$ $R^2 = 0.546$	$k_L = 0.0594$ $R^2 = 0.7938$
Pseudo second order model (PSOM) $\frac{t}{q_t} = \frac{1}{k_p q_e^2} + \frac{t}{q_e}$	$k_p = 0.1465$ $R^2 = 0.998$	$k_p = 0.0564$ $R^2 = 0.997$	$k_p = 0.0343$ $R^2 = 0.9984$

**Table 6**  
Results of analysis of different adsorption isotherms.

Adsorption isotherm model	Expression	Temperature 20 °C		Temperature 35 °C	
		Constants	R <sup>2</sup>	Constants	R <sup>2</sup>
Langmuir model	$q_e = \frac{K_L q^0 C_e}{1 + K_L C_e}$	$q^0 = 25.510$ $K_L = 0.888$	0.998	$q^0 = 1.250$ $K_L = 0.0380$	0.961
Freundlich model	$q_e = K_F C_e^{1/n_F}$	$K_F = 11.69$ $n_F = 1.996$	0.695	$K_F = 127.93$ $n_F = 0.5665$	0.930

pseudo-second-order and the rate limiting step is of chemisorption nature. Values of kinetic parameters are shown in Table 5.

3.3.2. Equilibrium study

Equilibrium studies have been performed at two different temperatures and data were fitted to two different adsorption isotherm models viz., Langmuir adsorption isotherm model and Freundlich adsorption isotherm model. The values of equilibrium constants are found out and shown in Table 6. Separation factor or equilibrium parameter ( $R_L$ ), as determined using the following equation  $R_L = \frac{1}{(1 + K_L C_0)}$  is an essential characteristics of Langmuir isotherm model [2,3,10]. In Fig. 9,  $R_L$  have been plotted against initial concentration at two different temperatures viz., 20 °C and 30 °C. It is evident from the figure that in all the cases  $R_L$  lies in the range of zero to one, ( $0 < R_L < 1$ ). This indicates that adsorption of MB on CCFP is favorable at the operating conditions being studied. The decrease in  $R_L$  values with increase in initial concentration of MB points out that removal is more favorable at higher initial concentration which is in conformity with the observation made by Hameed et al. [10]. The maximum removal capacity of CCFP for MB is found to be 25 mg/g as

evident from the value of  $q^0$ , Langmuir adsorption isotherm model parameter. This value is very much comparable with the other adsorbents when they were tested for MB removal by other scientists. The values are shown in Table 7.

3.3.3. Optimization of MB removal

To optimize process variables for removal of MB using CCFP, RSM is used. Three process parameters viz., initial concentration of MB, amount of adsorbent and pH of solution are considered as numeric factors and percentage removal of MB is considered as response. The optimum condition of MB removal and the interactive effect of these variables on the response function have been assessed using RSM.

The list of experiments as designed by RSM and the values of response (percentage removal of MB) for each sample obtained at corresponding experimental conditions are shown in Table 2. It is a common fact that pH affects the ionization and protonation of compounds, which are influential factors in adsorption process. But from Table 2 it is seen that 97.50% and 99.6225% MB removal have been achieved at pH 10.36 and 3.64 respectively when other parameters like weight of CCFP and initial concentration of MB are kept constant at 0.65 g and 20 mg/L respectively. Thus, it can be said that pH has a little effect on the removal process for the present system. This may be attributed to the superiority nature of the prepared adsorbent in terms of its porosity. Methylene Blue in its present concentration (20 mg/L) can be adsorbed to the pores of the

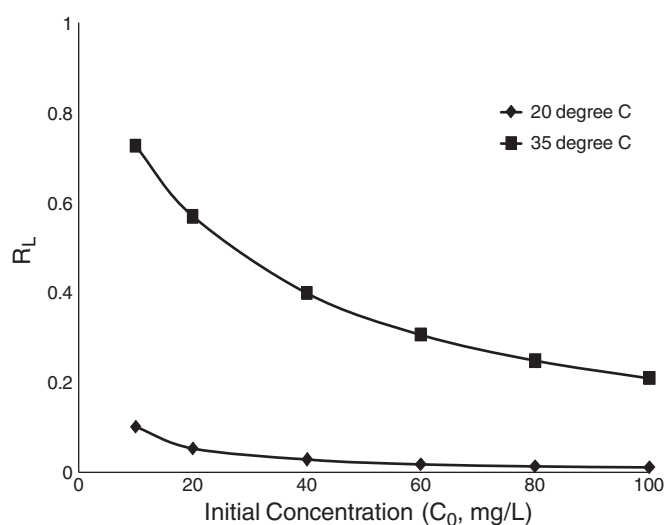


Fig. 9. Effect of initial concentration of MB on separation factor  $R_L$ .

**Table 7**  
Removal capacity of various adsorbents for Methylene Blue.

Type of adsorbents	Adsorption capacity (mg MB/g Adsorbent)	References
Jordanian tripoli	16.6	A. S. Alzaydien [11]
Rice husk activated carbon	9.83	Sharma et al. [12]
Activated carbon from <i>Delonix regia</i> pods	24.0	Ho et al. [13]
Coir pith carbon	5.87	Kavitha and Namasivayam [14]
Solid waste from leather industry	80	Oliveira et al. [15]
Rectorite	89.4	He et al. [16]
Fly ash	0.814	Khan et al. [17]
Lemon peel	29	Kumar and Porkodi [18]
Tamarind fruit shell	1.72	P. Saha [19]
Acid activated carbon	60.61	Arivoli et al. [20]

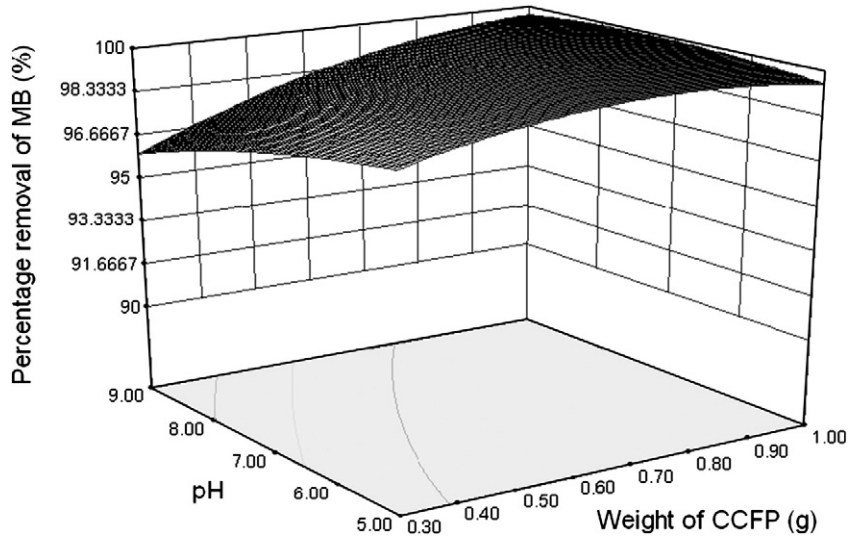


Fig. 10. Combined effect of pH and weight of CCFP on percentage removal of MB.

prepared adsorbent (CCFP) without being affected by the microenvironment of the process.

The regression analysis was performed to fit the response. To analyze the data, quadratic process order was selected but no transformation was required. The final regression function for MB removal in terms of coded factors is given below:

$$R_2 = 99.50 + 1.14*A' - 0.60*B' - 0.73*C' + 0.69*A'*B' + 0.48*A'*C' - 0.50*B'*C' - 0.73*A'^2 - 0.32*B'^2 - 0.27*C'^2 \quad (8)$$

where  $R_2$  = percentage removal of MB (%),  $A'$  = weight of CCFP (g),  $B'$  = pH,  $C'$  = initial concentration of MB (mg/L).

Analysis by ANOVA explores that all the three parameters have significant effect on removal of MB. Quadratic effect of weight of adsorbent, pH and initial concentration of MB were significant. The conjugated effect of weight of adsorbent and pH, weight of adsorbent and initial concentration of MB and conjugated effect of pH and initial concentration were reported as significant.

Fig. 10 shows the combined effect of weight and pH on adsorption of MB on CCFP at constant initial concentration of MB ( $C' = 20$  mg/L). It is evident from the figure that pH has a profound effect on removal of MB. With increase in pH, removal of MB decreases at lower weight of CCFP but at higher amount of CCFP, removal is almost constant with pH. At constant pH, removal increases with increase in weight of CCFP. It is quite obvious that when amount of adsorbent is high then removal is also high because available surface area for adsorption is much more.

Fig. 11 shows the three dimensional response surface of the combined effect of weight and initial concentration on percentage removal at constant pH ( $B' = 7$ ). With increase in initial concentration, removal decreases when weight of CCFP is kept constant. This is because at constant weight of CCFP when initial concentration of dye is increasing adsorbent gets saturated and it cannot adsorb further. Whereas with increase in weight of CCFP percent removal increases monotonously. The reason is that when weight of CCFP is more, then the surface area available is also high, that increases the percentage removal.

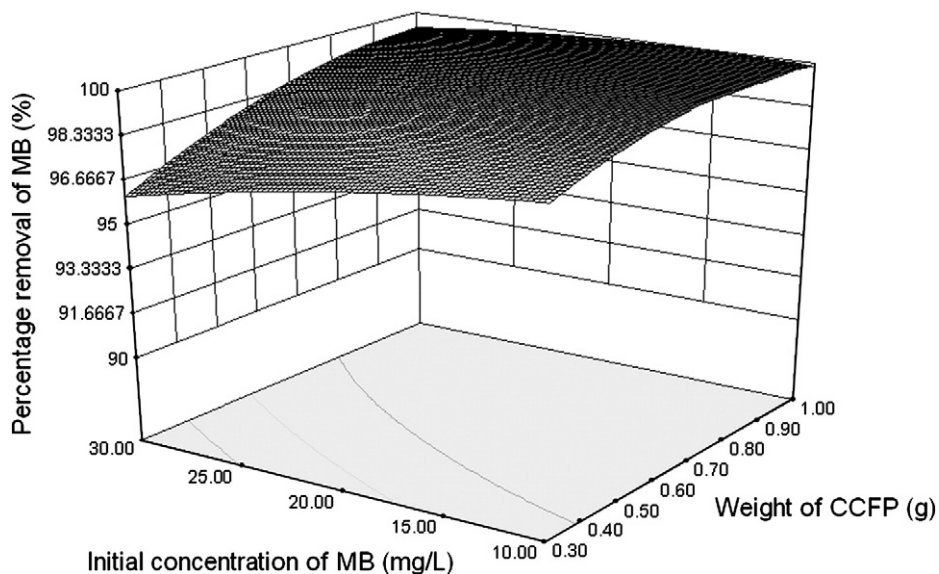


Fig. 11. Combined effect of initial concentration of MB and weight of CCFP on percentage removal of MB.

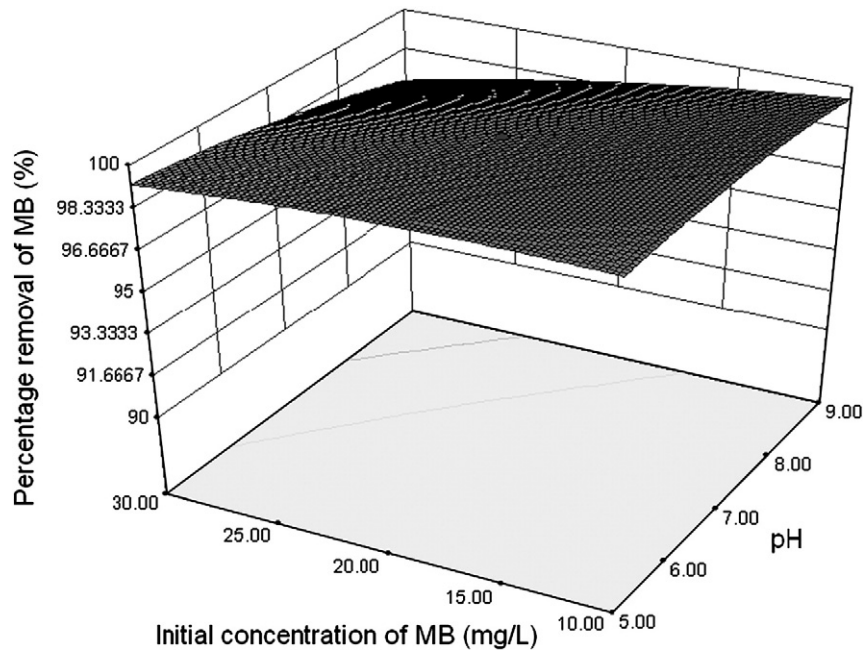


Fig. 12. Combined effect of initial concentration of MB and pH on percentage removal of MB.

Fig. 12 shows the three dimensional response surfaces of the combined effect of initial concentration and pH on percentage removal of dye at constant weight of CCFP ( $A' = 0.65$  g). It is evident from the figure that removal of MB decreases when initial concentration increases. Removal attains its maximum value when pH is low and initial concentration is also low.

The actual and predicted responses are shown in Fig. 13. Actual values are measured response data for a particular run and the predicted values are evaluated from the model. The statistical parameters obtained are shown in Table 8. The fair values of statistical parameters are due to the selection of different variables in wide ranges with a limited number of experiments. The best condition for removal of MB was optimized using Design Expert Software keeping pH at 7. According to the software the optimum response can be

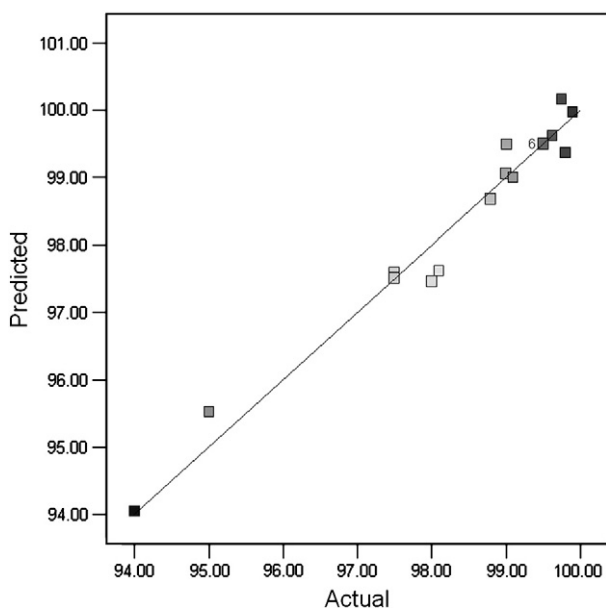


Fig. 13. Plot of actual response versus predicted response for removal of MB.

obtained when weight of CCFP, pH and initial concentration of MB were 0.48 g, 7 and 30 mg/L respectively. This has also been verified by experimentation. Predicted percentage removal of MB (97.5%) at the said condition matches very well with the experimental value (98.0%).

#### 4. Conclusion

A low cost adsorbent has been prepared by carbonizing citrus fruit peel, a waste material. The carbonization condition has been optimized using RSM and the sample obtained at this condition is termed as CCFP. To assess the efficacy of CCFP as an adsorbent, an extensive investigation has been performed with an aim to develop a new cutting edge technology for MB removal from its simulated solution by contacting the solution with CCFP in a batch contactor.

PSOM has been found to fit most satisfactorily. Maximum 99.08% removal was obtained during kinetic study in a batch contactor. The process condition for removal of MB has also been optimized by RSM. Finally, it can be stated that CCFP, having an excellent potential of adsorption of dye, can be efficiently used for treatment of industrial effluent containing other pollutants like heavy metals etc.

#### Nomenclature

- A Weight ratio as given in Eq. (4), (g/g).
- $A'$  Weight of adsorbent as given in Eq. (8), (g).
- B Temperature of carbonization as given in Eq. (4), ( $^{\circ}$ C).
- $B'$  pH as given in Eq. (8).
- C Time of carbonization as given in Eq. (4), (h).
- $C'$  Initial concentration of MB as given in Eq. (8), (mg/L).
- $C_0$  Initial concentration of MB as used in the expression of  $R_L$

Table 8  
Values of statistical parameter.

Statistical parameter	Values
R-squared	0.9704
Adj R-squared	0.9437
Pred R-squared	0.7547

$K_F$	Adsorption equilibrium constant used in Freundlich adsorption isotherm model, (mg adsorbate/g activated charcoal) (mg adsorbate/L)n.
$K_L$	Adsorption equilibrium constant used in Langmuir isotherm, (L/mg adsorbate).
$k_M$	Rate constant of intraparticle transport as used in Eq. (5), ( $\text{mg g}^{-1} \text{h}^{-1/2}$ ).
$k_L$	Overall rate constant as used in Eq. 6, ( $\text{h}^{-1}$ ).
$k_p$	Pseudo-second-order rate constant of sorption, ( $\text{g mg}^{-1} \text{h}^{-1}$ ).
$N$	Total number of experiments.
$n$	Number of variables.
$n_F$	Adsorption equilibrium constant used in Freundlich adsorption isotherm model.
$n_C$	Center point.
$q_t$	Solid phase concentration of adsorbate at time t, (mg/g).
$q_e$	Solid phase concentration of adsorbate at equilibrium, (mg/g).
$q^0$	Solid phase concentration of adsorbate for complete monolayer formation (mg/g).
$R_1$	Decolorizing power, (mg MB removed/g charred sample).
$R_2$	Percentage removal of MB (%).
$R_L$	Separation factor.
$t$	Time, (h).
$W$	Weight of CCFP as given in Fig. 7, (g).
$X_i$	Independent variables called factors.
$Y$	Response of the system.
$\alpha$	Distance of axial point from center.
$\beta_0$	Constant coefficient.
$\beta_i$	Linear coefficient.
$\beta_{ii}$	Quadratic coefficients.
$\beta_{ij}$	Interaction coefficient.

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