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A novel macrofungus for the biosorption of hazardous dye and its reuse potential: experimental design approach using response surface methodology

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ABSTRACT

In the present study, a novel biosorbent, namely *Agaricus campestris*, was used for the removal of Methylene Blue (MB) from an aqueous medium. The biosorbent was characterized using fourier-transform infrared spectrometer spectra, scanning electron microscopy-energy dispersive X-ray, and thermogravimetric analysis. The influence of important process parameters including pH (4–7), temperature (25°C–35°C), contact time (15–25 min), and biosorbent amount (40–80 mg) on the uptake of MB solution were also optimized, which significantly affected the removal efficiency of MB. A central composite design (CCD) combined with response surface modeling (RSM) was carried out to maximize MB removal by *A. campestris* for the adsorption process. A regression model was derived using RSM to predict the responses and analysis of variance (ANOVA), and to check model adequacy lack of fit test was used. The *A. campestris* adsorption capacity was determined as 24.2 mg g^{-1}. The ANOVA showed a high coefficient of determination (R^2 = 0.9987). This study clearly revealed that RSM was one of the most effective and appropriate method for the optimization of operating conditions. The possibility of reusing *A. campestris* was also investigated and, as a result, it was found quite possible and showed high performance in the recovery of MB.

Keywords: Methylene Blue; *Agaricus campestris;* Response surface modeling; Central composite design; Regression model

1. Introduction

Synthetic dyes, used in various industrial areas, are hazardous organic pollutants that are discharged into the environment, especially into aquatic areas. These dyes, used particularly in the textile, pharmaceutical, cosmetics, plastic, leather, paint, paper, and food industries, have been extensively studied due to their commercial importance and effect on environment [1–4]. It is estimated that approximately 20% of water-soluble dyes used in these industries remain in wastewater during the production process and are discharged into the ecosystem [5]. When released into aquatic areas, these dyes reduce the passage of sunlight to lower layers, reduce the amount of oxygen in water and harm the living organisms due to their toxicity. Thus, they negatively affect the aquatic life by creating anaerobic status and limiting aquatic organisms [6]. In addition, these dyes which contaminate both surface water and groundwater have carcinogenic, allergenic, and mutagenic effects [7–9] and can lead to fatal diseases in humans. Therefore, the treatment of wastewater containing synthetic dyes is of great importance. Various methods such as membrane separation, fungal decolorization, coagulation,

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biosorption, chemical oxidation, and adsorption [1,2,10–12] can be used for removal of dyes from industrial residues. However, these methods have certain drawbacks. Among these physicochemical methods, the adsorption technique which is an eco-friendly method is effective in the removal of synthetic dyes from wastewater as it is an inexpensive, flexible, and relatively simple process [13,14]. All of the aforementioned methods also use non-toxic adsorbents that show great removal performance. Therefore, biosorbents which are easily accessible, non-toxic, and inexpensive and have a high adsorption capacity are required for the removal of synthetic dyes from wastewater. In order to find the removal efficiency and maximum adsorption capacity of adsorbents, the process variables must be optimized. The optimization of the process variables by using conventional techniques is not preferred as a great number of experiments are required for the process and such techniques are expensive and time-consuming. The major disadvantage of these techniques is that the effects of the process variables on the dependent variable cannot be determined. These disadvantages can be eliminated by using a statistical experimental design approach, which not only reduces the number of experiments but also provides an appropriate model for the process optimization, which helps to evaluate the effects between the variables. In recent years, different experimental design methods have been preferred for the optimization of multivariate physicochemical process [15–17]. Response surface modeling (RSM) is an especially effective tool that has been used to understand the effects of several variables that influence the responses by varying them simultaneously and carrying out a limited number of experiments. As there are no studies examining Methylene Blue (MB) adsorption on *Agaricus campestris* (*A. campestris*) and the effects of the parameters affecting the adsorption, it was of great importance to use a new adsorbent and investigate the reuse potential of this adsorbent in this study. Within the scope of this study, *A. campestris* was used as a biosorbent for the removal of MB. The *A. campestris* is commonly known as the field fungus which belongs to the class of the Basidiomycetes. This mushroom is a white-rot fungus which can be consumed by humans. Mushrooms belonging to the class of Basidiomycetes are widely used in biotechnological studies due to their cell walls as the polysaccharides in their cell walls, in particular the chitin layer, has a high capacity of dye and metal binding [18,19]. Moreover, laccase is an extracellular enzyme which is synthesized by these fungi and plays an active role in the removal of some toxic dyes from wastewater. The aims of the present study are summarized as follows: (1) to obtain maximum adsorption capacity of *A. campestris* by using a central composite design (CCD) optimization approach, (2) to determine *A. campestris* adsorption capacity for MB and investigate the effect off used independent variables on MB adsorption, on the *A. campestris* surface and their interactions in MB dye removal, (3) to verify the validity of the proposed model by using ANOVA, (4) to investigate the reuse potential of the used biosorbent, and (5) to offer the best solution for maximum MB adsorption and other alternative solutions.

2. Experimental procedure

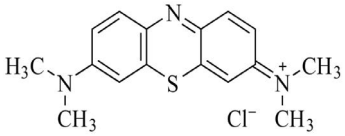
2.1. Chemicals and instruments

Methylene Blue (≥82%), sodium hydroxide (NaOH, ≥95%), and hydrochloric acid (HCl, 37%) were purchased from Merck Company (Darmstadt, Germany) and the used chemicals were commercially available and of analytical grade. Thermogravimetric analyses and differential thermal analyzer, fourier-transform infrared spectrometer (FTIR) spectra, surface morphology (SEM), and X-ray analysis of *A. campestris* and MB loaded *A. campestris* were performed using DTG-60 (Shimadzu, Japan), FTIR spectrophotometer with attenuated total reflectance (ATR; 67000, Japan), a digital SEM coupled with energy dispersive X-ray (EDX; Hitachi SU3500, Japan) and X-ray diffractometer (XRD; Rigaku MiniFlex-600, Japan), respectively. Ultrapure water was used in this study (ELGA LabWater/VWS; UK). An EZDO bench top PL-700PV model pH-meter was used for pH measurements and Wisd model shaking water bath was used for the batch adsorption experiments.

2.2. Preparation procedure of biosorbent and dye solutions

In present study, the mushrooms used as adsorbents were collected during 2016 spring season from the natural habitats in Tunceli, Turkey. Based on microscopic and macroscopic characteristics, their species were diagnosed. The samples were dried in a drying oven for 48 h at 40°C before being used as adsorbents. The dried samples were then floured with a muller and then sieved. Among the sized mushroom samples, those smaller than 120 meshes were used as adsorbents. Powdered mushroom samples were treated with 2 M NaOH besides 2 M HCl before used as adsorbent. The powdered samples were stored in glass jars until they were used. To obtain a calibration curve, firstly, 100 mL stock solution (1,000 mg L^{-1}) was prepared using ultrapure water and the lower concentrations were prepared by diluting this stock solution. The physicochemical characteristics of which are given in Table 1.

Table 1
Physicochemical characteristics of Methylene Blue

Name	Molecular structure	Molecular formula	M_w (g mol^{-1})	λ_{max} (nm)
Methylene Blue		$C_{16}H_{18}ClN_3S$	319.85	660

2.3. Analytical method

An experimental design set was created out to achieve MB removal from aqueous solutions. Using the MB standard solutions at concentrations from 0.5 to 10 mg L^{-1}, a calibration curve was created to calculate the adsorbed MB before the concentrations of the samples were determined. The amount of adsorbent determined by the experiment (Table 2) was added into 40 mL of the MB solution of initial concentration (10 mg L^{-1}) under conditions including pH (4–10), temperature (25°C–35°C), and contact time (15–25 min). To adjust the sample solution pH, HCl (0.05–0.1 N), and NaOH (0.05–0.1 N) were used. The solid was then separated from the filtrate by filtration (Macherey–Nagel Qualitative Filter Paper 110 mm) and the adsorbance of the filtrate was measured using UV-vis spectrophotometer set at 660 nm wavelength. The MB amount adsorbed by the unit mass of *A. campestris* was calculated using the following equation:

$$q = \frac{\left(C_0 - C_e\right)V}{m} \tag{1}$$

where q (mg g^{-1}), C_e (mg L^{-1}), and C_0 (mg L^{-1}) represent the equilibrium and initial concentrations of the MB solution, respectively. Similarly, m (g) represents the adsorbent's mass and V (L) refers to the solution volume.

2.4. CCD design and optimization

RSM provides various advantages one of which is determining the most appropriate operational process variables. It is also an empirical statistical technique that, when used, can reduce experimentation time, process variability, and most importantly overall cost [15,20,21]. CCD is widely used to obtain both a convenient second-order model and to examine the various synergetic effects of independent factors on responses. This method is preferred because the number of experiments needed to evaluate the main effect and the interactions of each parameter can be reduced [22]. The CCD is generally characterized by three operations: $2k$ axial runs, 2^k factorial runs, and central runs. As given in Table 2, a total of 30 experiments (axial points; 8, factorial points; 16 and replicates; 6 at the center) were designed using CCD within the scope of this study.

$$N = 2k + 2^k + n_c \tag{2}$$

where k and n_c represent the factor numbers and the center point numbers, respectively. Alpha (α), which depends on the number of rotational and factorial points, represents the distance from the center point of the axial point and can be calculated using the equation given below [23,24]:

$$\alpha = 2^{(k/4)} \tag{3}$$

This experimental design was conducted to minimize the effects of uncontrolled parameters and was based on controllable factors including pH (X_1), temperature (X_2), contact time (X_3), and adsorbent amount (X_4). The process variables and their interactions may be estimated by performing a minimum number of experiments using an experimental design created with CCD. In addition, the optimization procedure provides various advantages such as checking model adequacy, response predicting, and mathematical model coefficients estimation [25]. The CCD examines the response to the maximum area of all variables and identifies the optimum value region. A four-factor (coded as: –α, –1, 0, +1, and +α coded at five levels) CCD combined with RSM was used to determine the maximum MB biosorption by *A. campestris*. According to preliminary experiment studies, four critical parameters affecting MB adsorption were selected as independent variables and the biosorption of MB by *A. campestris* (Y) was considered as the dependent variable. A second-order polynomial equation was derived from the regression analysis and is presented as follows:

$$\begin{aligned} Y\left(\text{mgMB/gAC}\right) = {} & +54.66 + 1.57X_1 - 1.53X_2 - 0.45X_3 \\ & - 0.62X_4 + 0.04X_1X_2 - 0.04X_1X_3 - 6.86E - 0.03X_1X_4 \\ & + 0.03X_2X_3 - 2.02E - 0.03X_2X_4 - 1.18E - 0.03X_3X_4 \\ & - 0.10X_1^2 + 0.02X_2^2 + 1.27X_3^2 + 4.53X_4^2 \end{aligned} \tag{4}$$

In the optimization of the MB removal process, in order to determine the optimum point and achieve highest treatment performance, the best method was layout of the surface plot. Optimization results were verified under predicted optimal conditions by using experiments that identify CCD. The predicted values of the model that confirmed RSM efficiency were similar to the results of the corresponding experiments. According to the obtained data from the CCD experimental design, it can be said that CCD is the ideal approach to optimize the experimental variables when used for the removal of MB from aqueous media by *A. campestris*. Therefore, the difference between the experimental results and the predicted results can be ignored in the efficiency of the proposed quadratic models and in predicting the optimum conditions. For optimum MB removal, numerical optimization values were obtained as a pH of 7.9, temperature of 35°C, contact time of 25 min, and *A. campestris* amount of 20 mg. The experimental range of the independent variables and their levels of MB adsorption are shown in Table 2. The proposed regression model was derived by analyzing the experimental results using the Design Expert software program (Design Expert Version 10, Stat-Ease, USA). In Table 3, different parameters such as variable conditions, experimental values, and predicted values are listed. Diagnostic checking tests provided by ANOVA were used for the adequacy of the proposed model. In addition, the factors determined by quadratic models can simply be related to the responses. The determination coefficient of R^2 characterizes the appropriate polynomial model. Because the R^2 values, in the observed response values, provide a measure of how variability can be clarified by experimental factors and their interactions [16]. These analyzes were performed using Fisher's "*F*"-test and *p*-value.

2.5. Desirability function

Desirability is a useful approach for multiple response optimizations and for using the simultaneous optimization technique. The desirability function (DF), a common

Table 2
Experimental factors and levels in CCD

Factors	Levels			Star point α = 3	
	Low (–1)	Central (0)	High (+1)	–α	+α
(X_1) pH	4	7	10	1	13
(X_2) temperature (°C)	25	30	35	20	40
(X_3) contact time (min)	15	20	25	10	30
(X_4) adsorbent amount (mg)	40	60	80	20	100
Run	X_1	X_2	X_3	X_4	(mg g^{-1})
1	13	30	20	60	5.2
2	10	35	15	40	15.8
3	4	35	15	40	12.4
4	7	30	20	60	8.9
5	7	30	20	20	24.2
6	10	25	15	40	14.9
7	1	30	20	60	5.2
8	4	25	15	40	13.6
9	10	35	25	40	16.0
10	7	30	20	60	8.5
11	4	25	25	80	6.6
12	7	40	20	60	10.6
13	7	30	20	60	8.8
14	4	35	25	80	6.9
15	10	35	15	80	6.3
16	7	30	20	60	8.4
17	10	25	15	80	6.8
18	7	30	20	60	9.0
19	7	30	20	60	8.8
20	4	35	25	40	14.8
21	10	35	25	80	6.4
22	7	30	30	60	8.7
23	7	30	20	100	7.8
24	7	20	20	60	10.0
25	7	30	10	60	9.0
26	4	25	15	80	6.7
27	10	25	25	40	12.6
28	4	25	25	40	14.0
29	4	35	15	80	4.7
30	10	25	25	80	3.5

and established technique used to discover global optimal conditions based on Derringer's, was used for this procedure. The basic approach is to convert each response into an individual DF that varies over intervals. To create a function for each individual response (d_i), firstly, each predicted response (ν_i), and experimental response (ν_i) are converted, and then desirability (D) is determined as a global function. Desirability should be maximized after selecting the optimum value of the effective variables, taking into account the interaction variables. Firstly, the response (ν) is converted into a particular desirability function (df_i) in the range of "0" (d_i = 0, represents minimum applicability or completely undesirable response) to "1" (d_i = 1, represents ideal response or completely desirable). To determine the optimal conditions for MB removal, optimization was carried out according to DF. In the present study, desirability was obtained as 0.619. In addition, possible solutions for the removal of MB from aqueous media are listed with the highest "D-value" and presented in Table 4. Using geometrical mean, individual desirability scores (dis) were combined on a single overall (global) desirability (D), which was optimized to find the optimum set of input variables [26].

Table 3
Analysis of variance (ANOVA) for the quadratic polynomial model

Source	Sum of squares	df	Mean square	*F*-value	*p*-value Prob. > *F*	
Model	560.32	14	40.02	806.12	<0.0001	Significant
X_1-pH	0.27	1	0.27	5.50	0.0332	
X_2-temperature	1.33	1	1.33	26.83	0.0001	
X_3-contact time	0.045	1	0.045	0.91	0.3553	
X_4-ads amount	408.79	1	408.79	8,233.61	<0.0001	
X_1X_2	4.77	1	4.77	96.12	<0.0001	
X_1X_3	6.44	1	6.44	129.78	<0.0001	
X_1X_4	2.71	1	2.71	54.61	<0.0001	
X_2X_3	6.36	1	6.36	128.05	<0.0001	
X_2X_4	0.65	1	0.65	13.13	0.0025	
X_3X_4	0.22	1	0.22	4.46	0.0519	
X_1^2	21.20	1	21.20	426.97	<0.0001	
X_2^2	4.19	1	4.19	84.45	<0.0001	
X_3^2	0.028	1	0.028	0.56	0.4672	
X_4^2	89.95	1	89.95	1,811.62	<0.0001	
Residual	0.74	15	0.050			
Lack of fit	0.49	10	0.049	0.97	0.5501	Not significant
Pure error	0.25	5	0.051			
Cor. total	561.06	29				
R-squared	0.9987					
Adj. *R*-squared	0.9974					
Pred. *R*-squared	0.9943					

*$p < 0.01$ highly significant; $0.01 < p < 0.05$ significant; $p > 0.05$ not significant.

$$\mathrm{DF} = \left[df_1^{\nu_i} \times df_2^{\nu_i} \times df_n^{\nu_n} \right],\ 0 \ge \nu_i \ge 1 \left(i = 1,2,\ldots,n \right), \sum_{i=1}^{n} \nu_i = 1 \quad (5)$$

In Eq. (5) df_i indicates the response desirability $U_i (i = 1, 2,3,\ldots,n)$ and ν_i represents the responses importance. The following equation shows the individual desirability function for the *i*th characteristic [24].

$$df_i = \left(\frac{U - \alpha}{\beta - \alpha} \right)^{w_i} : \alpha \le U \le \beta \rightarrow \begin{matrix} df_i = 1, & U > \beta \\ df_i = 0, & U < \alpha \end{matrix} \quad (6)$$

3. Results and discussion

3.1. Characterization of the biosorbent

3.1.1. FTIR spectroscopy

The spectra of the pretreated *A. campestris* and the MB loaded *A. campestris* were compared (Fig. 1) by using FTIR. The spectra were recorded in the frequency range of 4,000–500 cm^{-1}. Fig. 1 shows the changes and shifts in the FTIR bands during the sorption of MB by *A. campestris*. Major changes were observed in the frequencies of 3,266; 2,922; 1,629; 1,376; and 1,020 cm^{-1}. These changes can be summarized as follows: the FTIR spectra of the MB loaded *A. campestris* showed a band around 3,266 cm^{-1} due to the presence of OH group and weak asymmetric stretching of C–H at 2,922 cm^{-1}. While the observed band was around 1,629 cm^{-1} strong symmetric and the band at 1,376 cm^{-1} the asymmetric stretching of C=O. The band for the MB loaded *A. campestris* can be assigned as 1,020 cm^{-1} (skeletal vibration of C–O). The natural *A. campestris* sample showed lower intensity peaks at 3,300; 2,900; 1,630; and at 1,020 cm^{-1} when compared with the MB loaded *A. campestris* sample, suggesting a disruption of some of these groups during the treatment.

3.1.2. Surface morphology and TGA

To characterize the surface morphology and fundamental physical properties of the adsorbent surfaces, scanning electron microscopy (SEM) micrographs have been a primary tool. They are useful in observing the appropriate size distribution, porosity, and particle shape of adsorbents. The morphological differences between the *A. campestris* and MB loaded *A. campestris* were proved by using SEM. These micrographs clearly indicated surface alterations in the *A. campestris* morphology before and after MB loading (Fig. 2). After being pretreated with MB, the surface of *A. campestris* became smoother which may be due to the MB sorption by *A. campestris*. The mineralogical composition of *A. campestris* was determined as 59.4% for C, 21.0% for O, 10.1% for K, 2.0% for P, 0.8% for Cl, 0.8% for

Table 4
Possible solution for MB removal conditions

Number	pH	Temperature	Contact time	Ads amount	R_1	Desirability	
1	7.72	35.0	25.0	40.0	16.30	0.619	Selected
2	7.63	35.0	24.9	40.0	16.30	0.619	
3	7.57	35.0	25.0	40.0	16.30	0.619	
4	7.78	34.9	25.0	40.0	16.29	0.619	
5	7.52	35.0	24.9	40.0	16.29	0.619	
6	7.43	35.0	24.9	40.0	16.28	0.618	
7	7.91	34.9	24.9	40.0	16.28	0.618	
8	7.75	35.0	24.8	40.0	16.27	0.618	
9	7.33	35.0	25.0	40.0	16.27	0.618	
10	7.99	35.0	24.7	40.0	16.26	0.617	
11	7.57	34.9	24.7	40.0	16.26	0.617	
12	7.67	34.9	24.6	40.0	16.26	0.617	

S, and 1.6% for CaO_2 using energy dispersive X-ray (EDX). The thermogravimetric analysis (TGA) results of *A. campestris* and MB loaded *A. campestris* is shown in Fig. 3. The TGA analysis was recorded in the temperature range of 25°C–800°C. It was observed that MB decomposition took place in the temperature range of 100.3°C–369.6°C. From this analysis, it was also observed that MB loaded *A. campestris* showed very similar degradation to *A. campestris*. Based on TGA analysis, it was found that MB loaded *A. campestris* had a low thermal stability. Results revealed that it is clear that no significant change was observed in the decomposition temperature of *A. campestris* and MB loaded *A. campestris*.

3.1.3. Second-order polynomial model

The results of ANOVA that contain the suggested second-order equation coefficients and model terms and a CCD program for the adsorption of MB by *A. campestris* are illustrated in Tables 2 and 3, respectively. As the Fisher test shows the larger *F*-values and the smaller *p*-values indicate more meaningful the proposed model terms, thus it was tested by using ANOVA. While *p*-values less than 0.05, it was indicated a significant regression in 95% confidence level, in addition, *F*-value is 806.12, indicating that the model is important. As "Prob. > *F*" values less than 0.05 indicate model terms are significant as statistically. In this case, X_1, X_2, X_4, X_1X_2, X_1X_3, X_1X_4, X_2X_3, X_2X_4, X_1^2, X_2^2, and X_4 are significant model terms but X_3, X_3X_4, and X_3^2 values greater than 0.05 indicate the model terms are not significant. The "lack-of-fit *p*-values" implies the "lack-of-fit" is not significant relating to the pure error, it measures the fitness of the model ($p > 0.05$). The "lack of fit *F*-value" of 0.97 implies the lack of fit is not significant relative to the pure error. In addition, number of experiments was sufficient to determine the effects of the independent variables for MB biosorption by *A. campestris*. This model goodness-of-fit was evaluated using determination coefficients (R^2) and determination adjusted coefficients (adj. R^2). Since it defines the percentage of variability in the response, it is desirable to have a high R^2 value of the proposed model and this value should be greater than 0.75 for validity of the model [16]. The obtained values of R^2 and adj. R^2 for the previously mentioned models are satisfactory. Because the model coefficient (R^2) was obtained as 0.9987, it can be said that 99.87% of the model-predicted values matched the experimental adsorbed MB values by *A. campestris*. By using residuals ($e = R_{exp} - R_{predic}$) assessment, model adequacy was investigated. There is a good concordance between predicted (R_{predic}) and experimental (R_{exp}) responses according to the residual analysis outlines. Additionally, when the normal probability plot is examined, it can be said that residuals distribution is normal and the model satisfies the assumptions of the ANOVA. The difference between the "pred. R^2; 0.9943" and "adj. R^2; 0.9974" is less than 0.2, it is clear that they are reasonably compatible. "Adeq. Precision" measures the signal to noise ratio and this ratio greater than 4 is desirable. The signal-to-noise ratio should be greater than 4 and it is measure by "Adeq. Precision". This study ratio is 130.626 and it indicates an adequate signal. The results expressed that using statistical model was adequate to predict of MB levels and was fitted to second-order polynomial equation.

3.2. RSM analysis

The effect of each parameter on the removal of MB from the aqueous solution and their interaction are presented in Fig. 4. As they were useful in determining response points including the maximum, middle, and minimum, three-dimensional (3D) response surface graphs were created according to the quadratic model. The impact of temperature and adsorbent amount on the removal of MB using *A. campestris* is illustrated in Fig. 4a. It is clear that the MB removal amount increased with the increase in temperature up to 35°C and decreased biosorbent amount. This showed that the removal of MB from the aqueous medium was strongly influenced by the biosorbent amount. Fig. 4b shows the 3D response surface of the influence of pH and biosorbent amount on the adsorption efficiency of MB on *A. campestris*. While it is clear that the biosorption amount of MB increased with the decrease of biosorbent dosage ($p < 0.01$) up to 40 mg, the pH change (from 4 to 10) showed a significant effect on MB adsorption

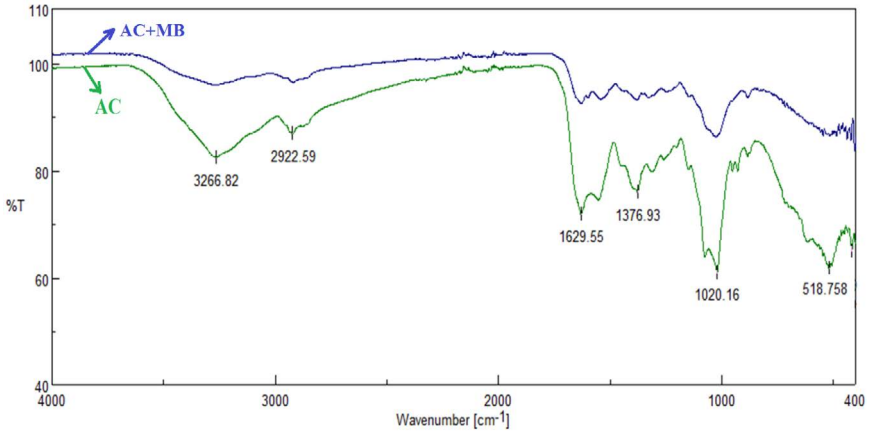


Fig. 1. FTIR spectra of *A. campestris* and MB loaded *A. campestris*.

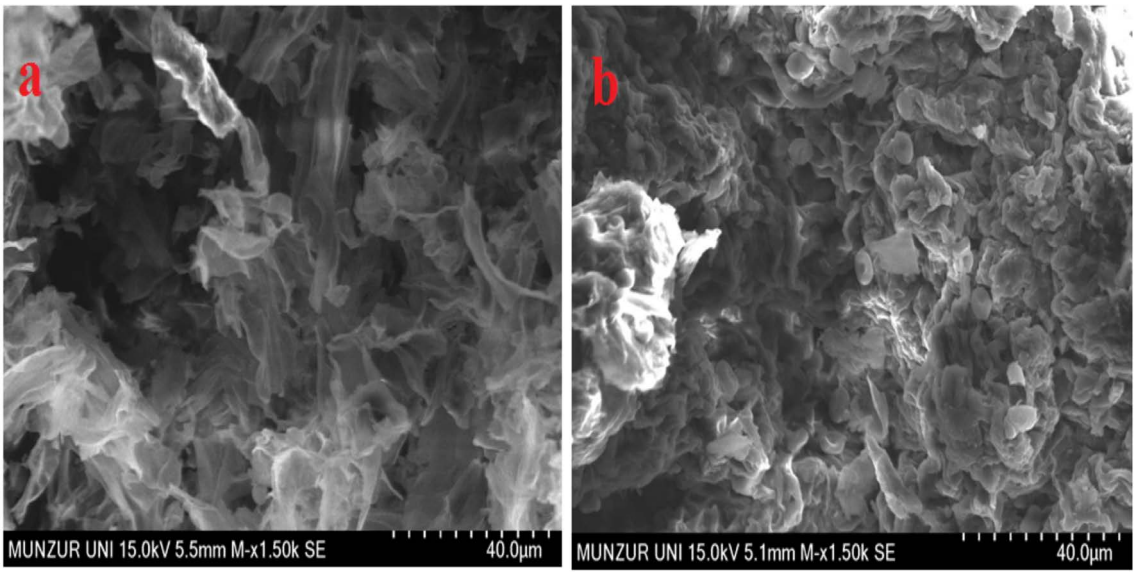


Fig. 2. SEM image of *A. campestris*: (a) before adsorption of MB and (b) after adsorption of MB.

($p < 0.01$). Fig. 4c represents the combined effect of contact time and biosorbent amount on MB removal at constant temperature and pH. It was observed that increasing the contact time did not have a significant effect on MB removal. However, the MB removal from aqueous media increased with the decrease in biosorbent amount. It can be said that, in the case of MB adsorption, the adsorbent amount is a more important factor than other adsorption parameters such as pH, contact time, and temperature.

3.3. Comparison of results

To support the optimized data obtained from numerical modeling under optimized conditions, obtained results were compared with the literature. In recent years, there have been a great number of studies in which different results were obtained using various adsorbents. Ai et al. [27] used a graphene nanosheet composite as an adsorbent to remove MB from water. They reported that this adsorbent showed an extraordinary adsorption capacity in the removal of MB. They stated that, based on kinetics and thermodynamics studies, this composite material could be utilized as an efficient adsorbent in the decontamination of the environment. de Oliveira Brito et al. [28] used raw Brazil nut shells as an adsorbent to remove MB from solutions. They obtained the maximal results of MB from the solution as 7.81 mg g^{-1} which they confirmed using the Langmuir model, pseudo-second-order kinetics, and thermodynamic studies. According to the results they obtained, this adsorbent can be useful in the removal of basic or acid dyes. Dil et al. [24] prepared a zinc oxide nanorods material and used it in the removal of crystal violet dye from aqueous solution adsorption technique. After optimized effective process parameters using design of experiments, crystal violet optimum removal efficiency was calculated as 99.82% under optimum conditions. According to ANOVA and Langmuir model, they obtained a high coefficient of determination (R^2, 0.992) and maximum adsorption capacity (113.64, mg g^{-1}).

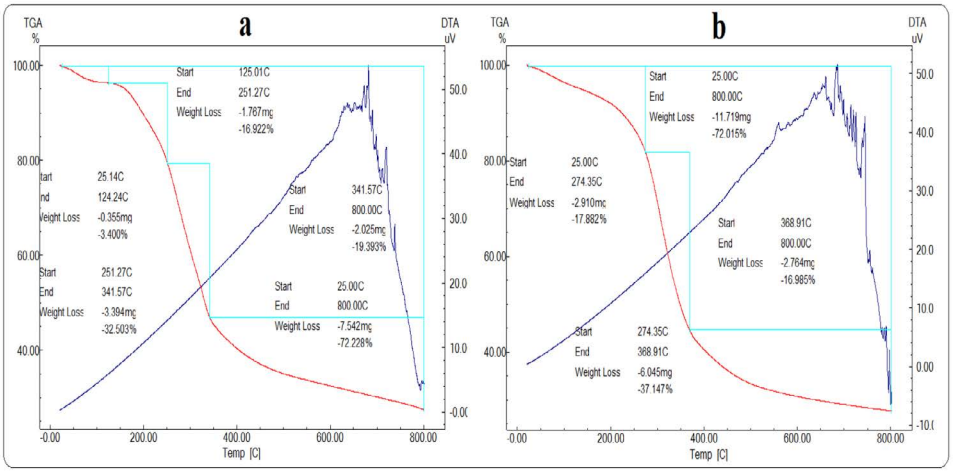


Fig. 3. TGA image of *A. campestris*: (a) before adsorption of MB and (b) after adsorption of MB.

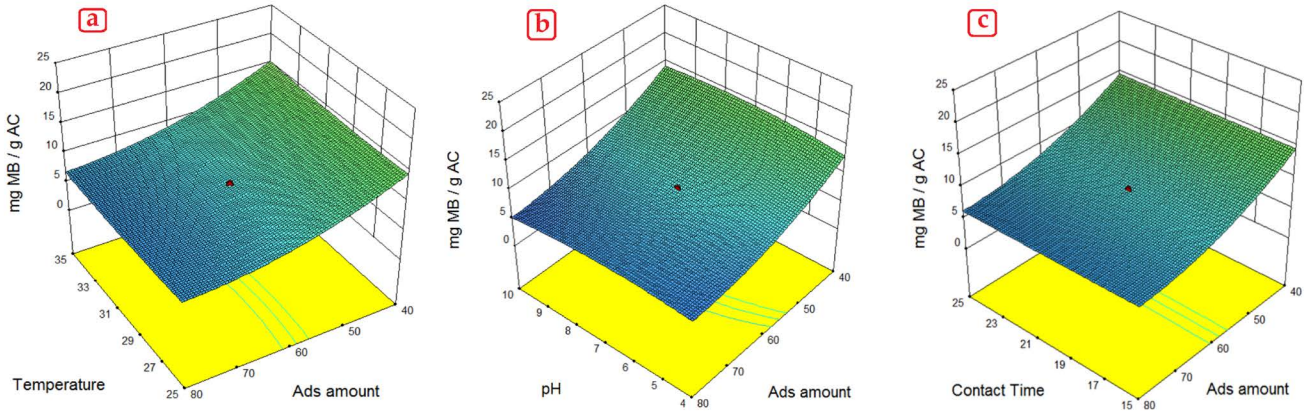


Fig. 4. 3D response surface graphs for MB sorption by *A. campestris* for interactive effect of: (a) temperature and adsorbent amount, (b) pH and adsorbent amount, and (c) contact time and adsorbent amount.

They also stated that RSM was one of the most appropriate methods to optimize the operating conditions [24]. A multi-wall carbon nanotube (MWCNT) nanocomposite was used as an adsorbent for the removal of orange II and sunset yellow FCF by Gao et al. [29]. Transmission electron microscopy, XRD, FTIR, and TGA were used for the characterization of MWCNT. They reported that while kinetics and isotherms studies were compatible with the Langmuir model, a low pH value favored the adsorption of these dyes [29]. Hameed [30] investigated feasibility of using papaya seeds for the removal of MB. After the effective adsorption parameters were investigated and optimized, adsorption isotherms such as Temkin and Freundlich were used to analyze the equilibrium data. Maximum adsorption capacity was obtained as 555.6 mg g^{-1} [30].

Mahapatra et al. [31] prepared activated carbon produced from the pyrolysis of sludge which was chemically activated using various agents and applied to remove MB. The activated carbon was characterized using FTIR and XRD. The iodine value of the activated carbon was determined and applied to MB adsorption. The maximum adsorption capacity of the activated carbon was found as 23.6 mg g^{-1} [31].

The present study was carried out using RSM with CCD model to optimize batch experimental studies for the removal of MB from aqueous solution. It was revealed that maximum adsorption of EBT occurred at the pH of 7.7, temperature 35°C, contact time of 25 min, and adsorbent amount of 20 mg. The *A. campestris* adsorption capacity was calculated as 24.2 mg g^{-1}. As a result of this study, it was found that *A. campestris* can be efficiently utilized as an adsorbent compared to various artificial and natural adsorbents as well as activated carbons due to the removal of MB from the aqueous solution when compared to the literature. Although various adsorbents have more adsorption capacities for MB than *A. campestris*, they have various disadvantages such as the some of them being artificial and that they may cause problems for the environment as secondary pollutants. Studies on MB removal are usually carried out with kinetic models or percentages of elimination. There are a limited number of studies to determine the adsorption capacity of using adsorbents. In the present study, *A. campestris* was used for the first time to demonstrate its high adsorption capacity in the removal of MB and was found advantageous as it is natural and environmentally friendly.

3.4. Desorption procedure and biosorbent reuse studies

Recovering the adsorbate after it has been used in an adsorption system and reusing it is desired as this reduces cost and proves that it is a qualified adsorbent. The process of desorption and reusing can destroy the adsorbent and, in particular, the biosorbents can be damaged due to their biological structure. Desorption studies also help to clarify the nature of the adsorption process. To understand whether desorption process is damaging the adsorbent used and to test the reusability of this adsorbent some experiments were carried out. Firstly, about 2.0 g of the adsorbent was treated with MB solution (10 mg L^{-1}, 1,000 mL) under optimum conditions that were determined using CCD. After the adsorption process, it was observed that MB was removed at a rate of approximately 99% from aqueous solution. For the elution of MB from the surface of *A. campestris*, various solvents (NaOH, HCl, and ethanol; 0.5 mol L^{-1}) was used for desorption and they were separated from the adsorbent by filtration. Separated absorbances of elution solvents were measured to understand whether they contained MB. It was observed that the desorption solvents eluted 99% of the adsorbed MB from the *A. campestris* surface. After the desorption, MB was again adsorbed on the *A. campestris* surface based on previous optimum conditions. This procedure was repeated at least 5 times and the percentage of desorption was found to be greater than 98%. The potential for repeated use of *A. campestris* was found to be good. As mentioned, *A. campestris* has a good regeneration and reusability ability, which is considered as an advantage in the removal of dye from industrial wastewater.

4. Conclusion

In this study, it has been researched whether *A. campestris*, which is an eco-friendly economic and edible biomaterial, can eliminate MB from the aqueous environment. In addition to the reusability potential of this biomaterial, experimental study design, and multi-parameter optimization were performed and the following results were obtained:

- A CCD optimization procedure was performed to reach a global optimal solution to maximize the adsorption of MB from aqueous media by *A. campestris*. To find a suitable model leading to optimum outcome conditions (pH: 7.7, temperature: 35°C, contact time: 25 min, and adsorbent amount: 20 mg), a CCD method was identified to yield a maximum MB removal of 99%.
- The proposed mathematical model provided a critical analysis for interactive influences of the selected independent variables on the MB adsorption process.
- The R^2 (0.9987) and adj R^2 (0.9974) values obtained via ANOVA were satisfactory. It can be said that 99.87% of the model-predicted values matched the experimental values of MB adsorbed by *A. campestris*.
- Based on the 3D plots, the percentage (%) of the removal of MB from aqueous solutions increased with the decrease in adsorbent amount and increase in temperature.
- The maximum *A. campestris* adsorption capacity was calculated as 24.2 mg MB g^{-1} *A. campestris*, in the experimental range of the variables.
- The obtained data confirmed that optimization is an effective approach for modeling the sorption process of MB to understand the relationships among the independent and response variables and to maximize the process efficiency.

In conclusion, the *A. campestris* that was prepared and used is a good candidate for the removal of azo dyes from aqueous media due to its adsorption capacity and reusability property.

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