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Biosorptive removal of Eriochrome Black-T using *Agaricus campestris*: Parameters optimization with response surface methodology

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ABSTRACT

In this study, Eriochrome Black T (EBT) removal from aqueous media by *Agaricus campestris* (AC) which is an eco-friendly biosorbent was investigated using a central composite design (CCD) combined with response surface methodology. The CCD was chosen as the statistical prediction method to reduce the number of experiments which, in turn, will directly save time and chemicals. To optimize the process, various experimental independent variables such as the pH of the solution, contact time, adsorbent dosage and temperature were selected. The optimal experimental conditions were obtained as 6.5, 30°C, 20 min and 20 mg, for solution pH, temperature, contact time and adsorbent dosage, respectively. Under these optimized conditions, maximum EBT (100 mg L^{-1} initial concentration) removal efficiency was calculated as 64.2 mg g^{-1}. The independent variables and their interaction significance were checked using analysis of variance and it was found that the EBT biosorption on AC was highly significant ($p < 0.001$). The results were justified by the relatively high correlation coefficients ($R^2 = 0.9967$) of the statistical prediction. The EBT biosorption was confirmed by fourier transform infrared spectroscopy (FTIR) analysis monitoring the functional groups during EBT biosorption on AC. This was the first report on the parameter optimization of EBT biosorption using AC in an experimental design. The used biosorbent was characterized by FTIR, scanning electron microscope coupled with energy dispersive spectrometer and thermogravimetric analysis. The proposed biosorption process efficiently removed EBT, present in various aqueous mediums and can be used in industrial processes.

Keywords: Eriochrome Black T; *Agaricus campestris*; Analysis of variance; Correlation coefficients; Experimental design

1. Introduction

Organic dyes or colorants, especially dyes classified as azo dyestuff, are the most used organic colorants in cosmetics, paper production and textile industries. When these dyes are released into bodies of water, they have negative effects on the environment. as they are not biodegradable compounds [1,2]. Due to being extremely resistant to temperature, light and microbial attacks, the removal of organic dyes is quite difficult [3–5]. Colored wastewater is a serious problem as it reduces light penetration and,

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therefore prevents the photosynthesis of water organisms and damages the esthetic structure of the water surface [6]. Eriochrome black-T (EBT) is classified as a dangerous dye due to its' chemical stability. This dye has been used as an indicator in titration and, complexation, in the textile industry and research laboratories [7,8]. However, because of its molecular form, the removal of EBT from aqueous mediums is highly difficult [9,10]. EBT has a greater resistance to photodegradation when it creates complex chemical structures with certain chemical reagents during the treatment of contaminated wastewater [11]. There are many contaminated water treatment methods in the literature in terms of the removal of dyes, including flotation, ion exchange, membrane filtration, coagulation and especially biosorption [12,13]. However, conventional techniques regarding the removal of dyes including chemical and biological processes are very expensive and can cause serious secondary pollution [14]. When compared with other techniques, the biosorption technique is the most effective as it can successfully remove synthetic dyes from effluents. Recently, in order to overcome environmental problems, energy shortage and increasing customer demands, scientists have been focused on finding a simple way to prepare new materials that can be effectively applicable in various areas [15]. For this purpose, various adsorbents have been tested to decrease dye concentrations from aqueous solutions [11,16,17]. Inexpensive and non-conventional adsorbents have attracted great interest in this regard. However, such adsorbents have high biosorption capacities. Therefore, developing adsorbents that are highly adsorptive, inexpensive, and readily available is a great concern. That is why, natural biomaterials have become a promising alternative due to their properties such as being low cost and eco-friendly.

In this study, *Agaricus campestris* (AC) was used as a biosorbent to remove EBT which is an environmental pollutant. AC is a white rot fungus belonging to the class of the Basidiomycetes. Basidiomycetes are used in many biotechnological studies [18–28], to remove hazardous pollutants from industrial wastes, especially for removal of textile dyes. Recently, several biotechnological approaches have been proposed for the removal of pollution sources by using bacteria or fungi [29–31]. The cell walls of macrofungi generally consist of chitin and other polysaccharides. Chitin is known to have high dye and metal binding capacity [32,33]. In addition, extracellular enzymes synthesized by white rot fungi are also involved in the decolorization of textile dyes, especially laccase. Various white rot fungi including *Trametes versicolor, Trametes modesta* and *Pleurotus eryngii* have been known to be used for the removal of textile dyes [34–38].

As far as it is known, there has been no research conducted on the biosorption potential of AC. This study focused on detecting EBT removal efficiency from aqueous media using AC. To minimize processing costs, focus was placed on the use of ecofriendly and inexpensive adsorbents and statistical methods such as central composite design (CCD) with response surface methodology (RSM). Traditional methods were not preferred due to the extra chemical consumption and excessive time spent for each parameter, as independent variable parameters must be changed by keeping all other variable values constant in these methods. This study focused on various process conditions to optimize a specific method. RSM based on CCD was selected for experimental studies to determine and optimize the effects of the process conditions on the response, which is the EBT amount adsorbed by AC. A response surface analysis was performed to understand which experimental conditions, along with their interactions, played a vital role in EBT adsorption by AC. The aim of present study can be summarized as follows: (1) to optimize the selected variables including pH and temperature for the removal of EBT from aqueous media; (2) to determine the maximum biosorption capacity of AC using an experimental design model; (3) to verify the validity of the proposed model by using ANOVA; and (4) to offer the best solution for maximum EBT biosorption by AC and other possible biosorbents.

2. Materials and methods

2.1. Instrumentation

Ultrapure water (ELGA LabWater/VWS, UK) was used in the experiments. An EZDO PL-700PV Bench (Taiwan) pH meter was used for pH measurements and a Wisd model (Germany) shaking water bath was used for batch biosorption experiments. The morphology of AC and EBT-loaded AC were characterized using a digital scanning electron microscope (SEM) coupled with energy dispersive spectrometer (EDS) (Hitachi SU3500, Japan). The AC and EBT-loaded AC were characterized with fourier transform infrared spectroscopy (FTIR), attenuated total reflectance (ATR; Jasco, 67000, Japan) and X-ray diffractometer (XRD; Rigaku MiniFlex-600, Japan) was used for the characterization of the AC and EBT-loaded AC for their morphological information. Thermogravimetric analyses (TGA) of AC and EBT-loaded AC were performed using a simultaneous thermogravimetric and differential thermal analyzer (DTG-60, Shimadzu, Japan).

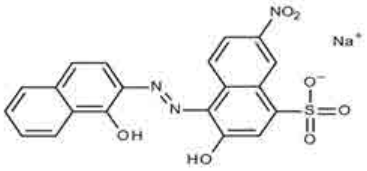
2.2. Preparation of the biosorbent

The mushroom samples (AC) used in the present study were collected during spring 2016 from Tunceli, a city located in the east of Turkey. Their species were determined based on their microscopic and macroscopic characteristics. The forest and soil debris were cleaned off the samples using a brush and, the samples were then transported to the laboratory. The fruit bodies of the mushroom samples were divided into several parts with a plastic knife and dried in an oven for 48 h at 40°C before the experimental studies. The dried samples were then grinded with muller and sieved. The powdered mushroom samples were stored in glass jars until they were used. The powdered mushroom samples were treated with 2 M NaOH in addition to 2 M HCl before they were used as adsorbents.

2.3. Preparation of dye solutions

The EBT (99%) was of analytical grade. Its' physicochemical characteristics are given in Table 1. The EBT stock solution (1,000 mg L^{-1}, Merck, Germany) was prepared by being dissolved in ultrapure water, and the other solutions were prepared from stock solution by dilution. To adjust the pH

Table 1
Physicochemical characteristics and global solutions for EBT removal

Name	Molecular structure	Molecular formula	M_w (g mol^{-1})	λ_{max} (nm)
Eriochrome Black T (Mordant Black 11)		$C_{20}H_{12}N_3O_7SNa$	461.38	530

pH	Temperature	Contact time	Ads dosage	Response	Desirability	
6.45	27.79	21.63	64.43	19.34	1.00	Selected
5.00	35.00	15.00	80.00	20.80	1.00	
8.00	25.00	15.00	80.00	16.04	1.00	
5.00	25.00	25.00	40.00	44.27	1.00	
8.00	35.00	15.00	40.00	35.17	1.00	
5.00	35.00	25.00	40.00	48.71	1.00	
5.00	25.00	25.00	80.00	19.67	1.00	
6.50	30.00	20.00	60.00	21.57	1.00	
5.00	35.00	25.00	80.00	22.16	1.00	
8.00	25.00	25.00	80.00	16.58	1.00	
5.00	25.00	15.00	80.00	19.42	1.00	
8.00	25.00	15.00	40.00	32.78	1.00	
5.00	35.00	15.00	40.00	48.10	1.00	
8.00	25.00	25.00	40.00	32.58	1.00	
8.00	35.00	25.00	80.00	18.13	1.00	
8.00	35.00	25.00	40.00	36.08	1.00	
5.00	25.00	15.00	40.00	44.78	1.00	
5.82	25.34	17.34	41.40	38.34	1.00	
5.94	29.52	16.89	53.90	27.41	1.00	
6.33	25.23	17.34	61.68	20.79	1.00	
7.39	27.55	15.99	45.66	29.15	1.00	
6.92	31.90	18.15	43.45	33.29	1.00	
5.39	28.95	22.39	53.17	29.98	1.00	
5.35	32.02	18.63	69.03	21.25	1.00	
6.59	32.24	24.07	48.96	30.54	1.00	

of the EBT solution, HCl (0.1 N) and NaOH (0.1 N) (Merck, Germany) were used.

2.4. Analytical method

An UV–Vis spectrophotometer set at 530 nm was used to measure the adsorbed EBT amount by AC. A calibration curve was created using the EBT dye solutions with known concentrations ranging from 2 to 100 mg L^{-1} to calculate the adsorbed EBT amount before the concentrations of the samples' were determined. The obtained calibration curve equation and R-squared value are shown as follows:

$$y = 0.0366x + 01849; \quad R^2 = 0.9996 \tag{1}$$

The experimental studies were performed based on CCD identified in Table 2. To optimize the variables, confirmative experiments were carried out with the parameters suggested by the CCD model (pH 5–8; temperature 25°C–35°C; contact time 25–35 min and adsorbent dose 40–80 mg). The obtained calibration curve was used to calculate the adsorbed EBT amount by AC.

2.5. Central composite design and optimization

RSM, an empirical statistical technique, was used to construct a regression model and an experimental study model designed to determine experimental conditions [39–42]. Determining the optimum process variables with a statistical technique provides various advantages including saving time. When biosorption processes are carried out using statistical experimental design, experimentation time, process variability and most importantly the overall cost can be reduced [43,44]. The CCD has been widely performed to fit a second-order model and to perform an experimental study with a minimum number of experiments. In this study, the

CCD approach was used for the optimization of the biosorption process variables and in order to decide the number of the biosorption experiments. Since the number of the independent variables was determined to be 4, the number of experiments in the experimental work plan with CCD was obtained as 30. Based on the preliminary experiments, the range of the process variables was defined and coded as ±1, 0 and ±α for the factorial points, the center points and the axial points, respectively [45].

The greatest advantage of CCD is that it is possible to estimate the interactions and effects of variables by performing a minimum number of experiments. The adequacy of the model, estimating the mathematical model coefficients and predicting the response were ensured by the optimization procedure [46]. In addition, this model helps to investigate the response on the entire variable domain and identify the region with the optimum value.

A five-level four-factor (each of the factors is coded at five levels as: -α, -1, 0, +1 and +α) CCD combined with RSM was used to determine maximum EBT biosorption by AC. The four critical parameters affecting EBT biosorption, namely pH (X_1), temperature (X_2), contact time (X_3), and adsorbent dosage (X_4) were selected as the independent variables. Biosorption removal amount (Y) was considered as the dependent variable based on the preliminary experiments. A second-order polynomial equation was derived from the regression analysis and is shown as follows:

$$Y\ (\text{mg EBT/g AC}) = 191.08 - 12.57X_1 - 0.88X_2 - 2.09X_3 - 2.46X_4 - 0.03X_1X_2 + 0.01X_1X_3 + 0.07X_1X_4 + 0.01X_2X_3 - 4.86X_2X_4 + 1.87X_3X_4 + 0.48X_1^2 + 0.02X_2^2 + 0.04X_3^2 + 0.01X_4^2 \quad (2)$$

The experimental range of the independent variables' and their levels of EBT biosorption are shown in Table 2. To analyze the experimental results, Design-Expert software program (Design-Expert Version 10, Stat-Ease, USA) was used and a regression model was proposed. Different parameters such as variable conditions, run order, experimental values and predicted values are listed in Table 2. The responses can be simply concerned with the selected factors by quadratic models in the optimization process. In the present study, a total of 30 experiments were carried out randomly arranged and the experimental study was completed. The proposed regression model that was derived using RSM to predict the adequacy of the responses was checked by means of tests such as ANOVA and a lack of fit test. The coefficients of determination such as R^2 and Adj R^2 are indicative of the appropriateness of the polynomial model, as they provide variability in observed response values, experimental factors and their interaction with each other [47]. All analyses were performed by using agency of Fisher's 'F'-test and p value. The four main parameter levels that were investigated according to the results of this study are presented in Table 3.

3. Results and discussion

3.1. Characterization

3.1.1. FTIR spectroscopy

The FTIR spectrum of the pretreated AC was compared with the FTIR of spiked with EBT-loaded AC. The spectra were recorded in a frequency range between 4,000 and 500 cm^{-1} (Table 4). The samples were analyzed with ATR. The FTIR spectrum of the EBT-loaded AC showed a band around 3,266 cm^{-1} due to the presence of hydroxyl group (OH) and at 2,922 cm^{-1} due to the weak asymmetric stretching of C–H. While band was determined around 1,630 cm^{-1} due to the strong symmetric and asymmetric stretching of C=O, a band at 1,376 cm^{-1}, was detected due to C–$(CH_3)_2$ bending. The band for the EBT-loaded AC can be assigned as 1,020 cm^{-1} (skeletal vibration of C–O). The AC sample showed lower intensity peaks at 3,300; 2,900; 1,630; and 1,020 cm^{-1} compared with the EBT-loaded AC sample, suggesting a disruption of some of these groups during treatment. Fig. 1 summarizes the shifts and changes in the FTIR bands during EBT sorption by AC.

3.1.2. Surface morphology

The morphological differences between the AC and EBT-loaded AC were proved by using SEM. In SEM images given in Fig. 2, the differences between the surface morphologies of AC and EBT-loaded AC can be clearly seen. After being pretreated with EBT, the surface of the AC was smoother, which may be due to the biosorption of EBT by AC. Thus it can be said that AC is good for EBT biosorption.

The mineralogical composition of AC was determined using EDS as 59.4% for C, 21.0% for oxygen (O), 10.1% for potassium (K), 2.0% for phosphorus (P), 0.8% for chlorine (Cl), 0.8% for sulfur (S) and 1.6% for calcium peroxide (CaO_2).

3.1.3. Thermogravimetric analysis

The TGA of AC and EBT-loaded AC is shown in Fig. 3. The TGA analysis was recorded in the temperature range of 25°C–800°C. It was observed that EBT decomposition took place in the temperature range of 100.3°C–369.6°C. From this analysis, it was determined that EBT-loaded AC shows very similar degradation with AC. From the TGA analysis, it is found that the EBT-loaded AC had a low thermal stability. Furthermore, no significant change was observed in the decomposition temperature of AC and EBT-loaded AC as a result of the TGA.

3.2. Second-order polynomial model

CCD combined with RSM and the ANOVA results of the conditions of EBT biosorption by AC are shown in Table 2 and Table 3, respectively. The model F-value of 323.15 shows that the model is significant. As "Prob > F" values less than 0.05 indicate that the model terms are statistically significant. In this case, X_1, X_2, X_4, X_1X_4, X_1^2, X_2^2, X_3^2 and X_4^2 were determined as significant model terms. Similarly, the X_3, X_1X_2, X_1X_3, X_2X_3, X_2X_4, and X_3X_4 which had values greater than 0.05 indicate that they were not significant. Because the model coefficient (R^2) was obtained as 0.9967, it can be said that 99.67% of the model-predicted values (Fig. 4) matched the experimental adsorbed EBT amount by AC. In addition, Ince and Kaplan Ince [47] reported that when $R^2 > 0.75$, the model is adequate. The "Adeq Precision" value, which measures the signal to noise ratio, is desired to be greater than 4. This ratio was obtained as 71.647 in the present study. At the same time, the difference between "Pred R-Squared (0.9826)"

Table 2
Experimental factors and levels in the CCD

Factors	Levels			Star point α = 1.5	
	Low (–1)	Central (0)	High (+1)	$-\alpha$	$+\alpha$
(X_1) pH	5	6.5	8	3.5	9.5
(X_2) Temperature (°C)	25	30	35	20	40
(X_3) Contact time (min)	15	20	25	10	30
(X_4) Adsorbent dosage (mg)	40	60	80	20	100
Run	X_1	X_2	X_3	X_4	(mg g^{-1})
1	5	35	15	80	21.3
2	5	25	15	80	20.1
3	6.5	30	30	60	25.4
4	8	35	25	80	17.8
5	5	25	25	40	45.6
6	5	25	15	40	44.9
7	8	25	15	40	32.1
8	5	35	25	40	48.7
9	8	25	25	80	17.4
10	6.5	30	20	60	21.7
11	6.5	30	20	60	20.5
12	8	35	15	80	15.9
13	8	25	15	80	15.8
14	8	25	25	40	31.9
15	5	25	25	80	19.3
16	3.5	30	20	60	32.4
17	6.5	20	20	60	21.4
18	5	35	25	80	23.7
19	6.5	30	10	60	25.4
20	6.5	30	20	100	20.1
21	8	35	25	40	36.2
22	6.5	30	20	60	21.8
23	6.5	40	20	60	25.8
24	6.5	30	20	20	64.2
25	8	35	15	40	35.4
26	5	35	15	40	48.1
27	6.5	30	20	60	21.8
28	6.5	30	20	60	21.6
29	9.5	30	20	60	18.9
30	6.5	30	20	60	21.9

and "Adj R-Squared (0.9936) " was less than 0.2, which is an expected result for a good model. There was also good agreement between these two coefficients because the difference was less than 0.2. The fit of the model was measured by the "Lack of Fit F-value" and the model is considered significant if its value is greater than $p > 0.05$. This study revealed that the fitness of the model was not significant as the "Lack of Fit F-value" was determined as 3.76 and therefore not statistically significant ($p > 0.05$). In addition, the number of experiments in the experimental design was adequate to determine the effects of the independent variables on EBT sorption by AC. The results expressed that using the statistical model was adequate to predict EBT levels and was fitted to the second-order polynomial equation. In this case, while X_1, X_2, X_4, X_1X_4, X_1^2, X_2^2, X_3^2, X_4^2 were highly significant ($p < 0.01$) X_3, X_1X_2, X_1X_3, X_2X_3 and X_2X_4, were significant model terms for EBT biosorption by AC.

3.3. RSM analysis

Response surface graphs were created as they are useful in determining response points including the maximum, minimum, and middle points in both two-dimensional (2D) and three-dimensional (3D) contour plots. Contour plots make it possible to determine the level of the variables and contribute to the desired response and also variables levels are plotted in a curve with equal response. Therefore, 2D plots are easier to interpret. Fig. 5 represents the 3D and

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

	Sum of		Mean	F	*p*-value	
Source	squares	df	square	Value	Prob > F	
Model	4,067.16	14	290.51	323.15	<0.0001	Significant
X_1-pH	384.80	1	384.80	428.03	<0.0001	
X_2-Temperature	35.62	1	35.62	39.63	<0.0001	
X_3-Contact time	2.00	1	2.00	2.22	0.1570	
X_4-Ads dosage	2,811.90	1	2,811.90	3,127.81	<0.0001	
$X_1 X_2$	0.87	1	0.87	0.97	0.3397	
$X_1 X_3$	0.090	1	0.090	0.10	0.7561	
$X_1 X_4$	74.05	1	74.05	82.36	<0.0001	
$X_2 X_3$	1.23	1	1.23	1.37	0.2600	
$X_2 X_4$	3.78	1	3.78	4.21	0.0581	
$X_3 X_4$	0.56	1	0.56	0.63	0.4413	
X_1^2	32.96	1	32.96	36.67	<0.0001	
X_2^2	9.23	1	9.23	10.26	0,0059	
X_3^2	28.89	1	28.89	32.13	<0.0001	
X_4^2	745.60	1	745.60	829.36	<0.0001	
Residual	13.48	15	0.90			
Lack of fit	11.90	10	1.19	3.76	0.0782	Not significant
Pure Error	1.58	5	0.32			
Cor Total	4,080.65	29				
R-Squared	0.9967					
Adj R-Squared	0.9936					
Pred R-Squared	0.9826					

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

Table 4
Instrumental parameters for FTIR analysis

Wavelength range	4,000–500 cm^{-1}
Spectral resolution	4 cm^{-1}
Crystal type	Diamond

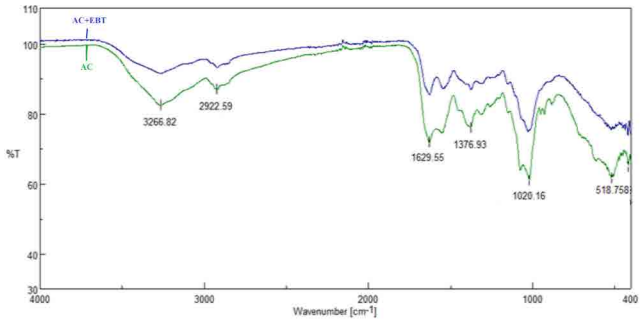


Fig. 1. FTIR spectra of AC and EBT-loaded AC.

2D response surface of the influence of pH and adsorbent dosage ($p < 0.0001$) on the biosorption efficiency of EBT dye by AC. While, it is evident that the biosorption amount of EBT increased up to 40 mg with the decrease of adsorbent dosage ($p < 0.01$), the pH change (from 3.5 to 9.5) showed a significant effect on EBT biosorption ($p < 0.01$). Fig. 6 shows the effects of temperature and adsorbent dosage ($p > 0.05$) on EBT removal at constant pH and contact time, with increased temperature, removal increases under other conditions. It can be seen in the figure that, when the adsorbent dosage increases, EBT removal from the aqueous media decreases. This is due to the fact that, at a higher solution temperature, the EBT removal amount increases based on the kinetic interaction. Therefore, the interaction of dye and adsorbent becomes high with increasing temperature. The removal amount of EBT dependency as contact time and adsorbent doses function is shown in Fig. 7 by using 3D graphs. While the adsorbent amount decreased, the removal amount of EBT dye increased ($p < 0.0001$). Depending on adsorbent amount, the biosorption of EBT significantly increased. The adsorbent amount is more important factor than the other biosorption parameters including pH, contact time and temperature in the case of EBT biosorption. In summary, all variables except contact time are effective on the removal of EBT from aqueous media, while the most effective of the dual interactions of the variables are pH–adsorbent dosage, temperature–adsorbent dosage and contact time–adsorbent dose. On the other hand, no significant change was observed in the 3D graphs of pH–temperature interactions, pH–contact time interactions and contact time–temperature interactions.

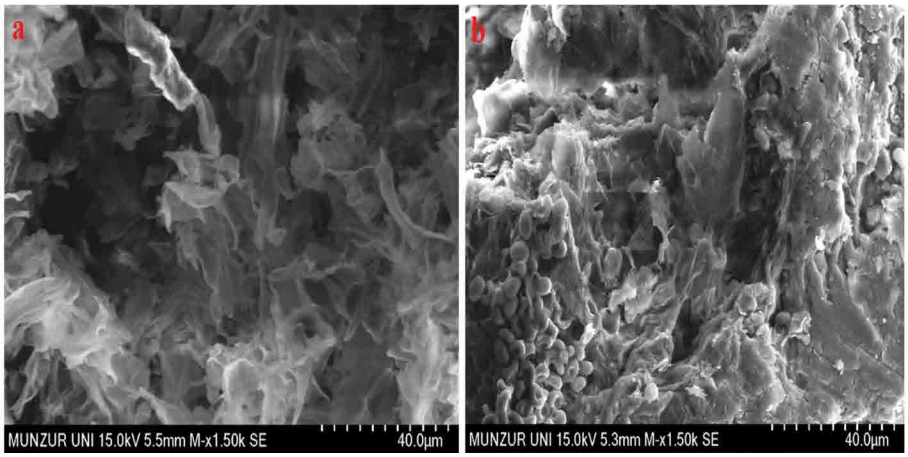


Fig. 2. SEM image of AC: (a) before the adsorption of EBT and (b) after the biosorption of EBT.

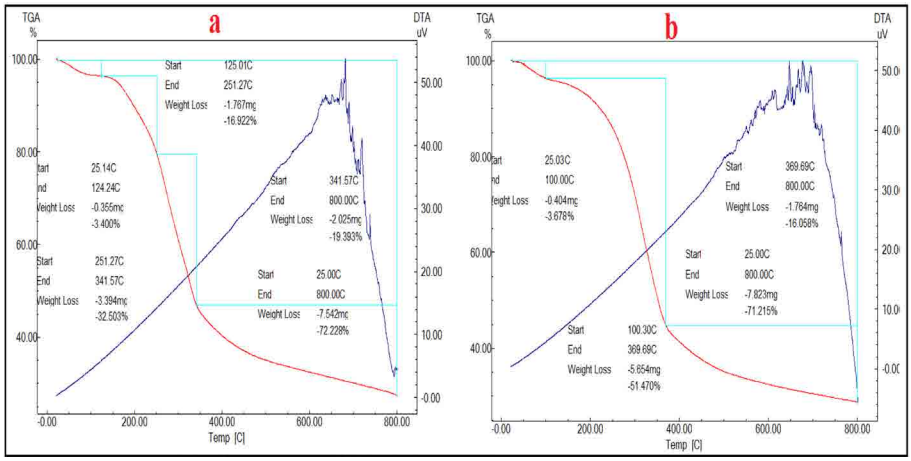


Fig. 3. TGA image of AC: (a) before the adsorption of EBT and (b) after the biosorption of EBT.

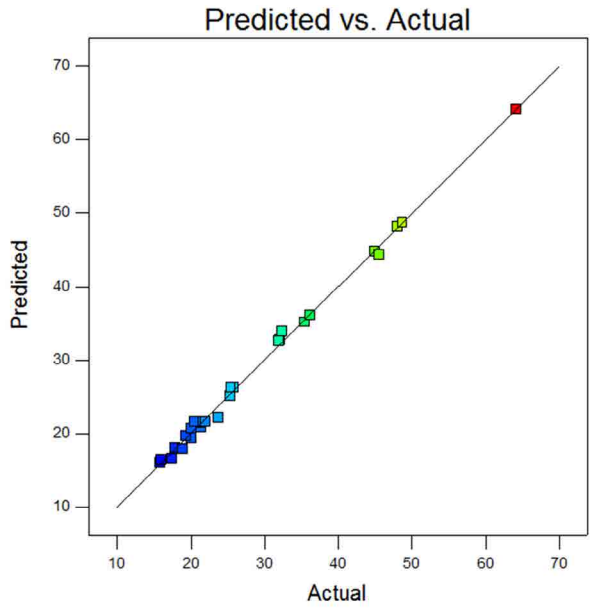


Fig. 4. Predicted and actual values of the experimental design.

3.4. Confirmation experiments

To support the data obtained from the model, the confirmative experiments were carried out with the parameters suggested by the model under optimized conditions (pH of 6.5, temperature of 30°C, contact time of 20 min and adsorbent dose of 20 mg) and the EBT removal percentage was found to be approximately 100%. Recently, there have been a great number of studies regarding EBT removal using various adsorbents and different results have been reported. Lee et al. [48] utilized RSM based on CCD to optimize independent variables including solution pH, ZnO dosage and EBT initial concentration that fairly influenced the EBT removal efficiency. Under the ideal experimental conditions, the conformity of the developed model was evaluated using ANOVA and, based on the suggested method, most of the EBT (83%) was colored by ZnO. In addition, concentration of EBT and reaction medium pH value played a vital role for EBT photocatalytic-mineralization. De Luna et al. [8] used activated carbon obtained from rice hull to remove EBT from aqueous solutions and calculated the percentage of the removed dye. After the process parameters were optimized using a Box–Behnken design, they obtained R^2 as

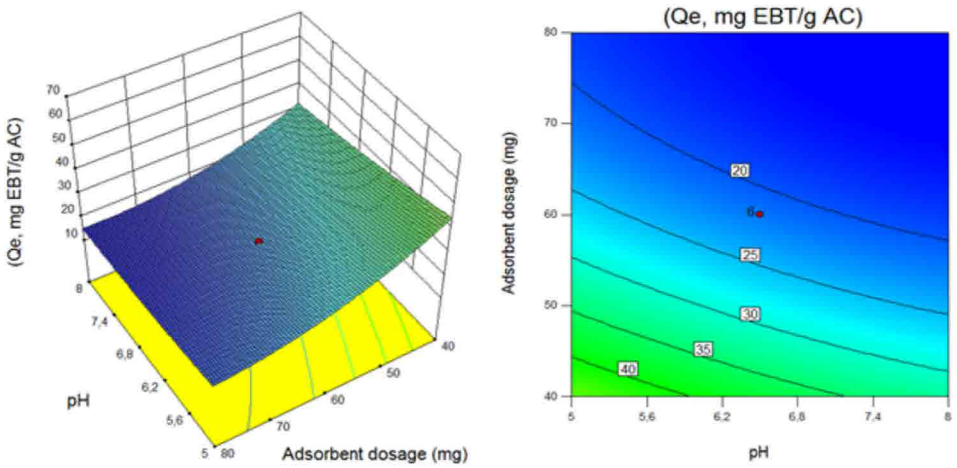


Fig. 5. Response surface and contour plot for EBT biosorption by AC as pH and adsorbent dosage.

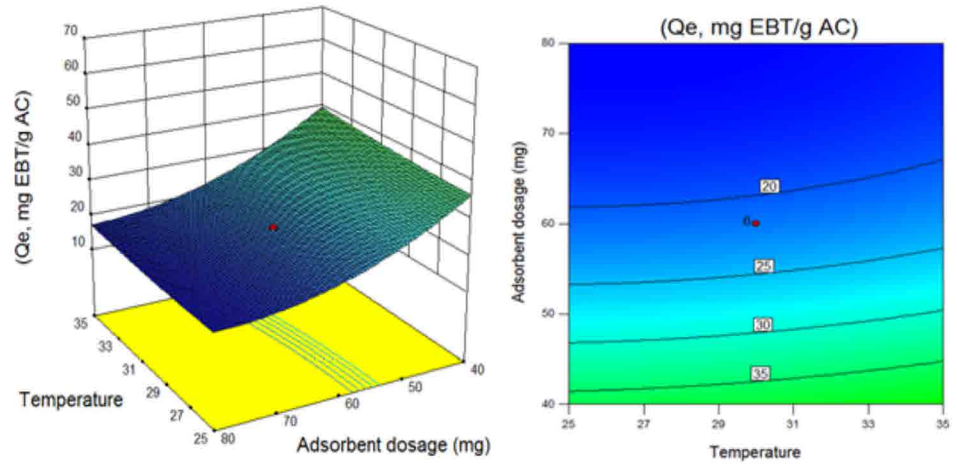


Fig. 6. Response surface and contour plot for EBT biosorption by AC as temperature and adsorbent dosage.

0.9996 based on the isotherm and kinetic studies including the Freundlich model.

Dave et al. [49] used eucalyptus bark as an adsorbent to remove EBT from aqueous media using batch experiments. They investigated various experimental parameters including temperature and solution pH to obtain kinetic and thermodynamic parameters. In addition, they designed a fixed-bed column to calculate a mass transfer kinetic approach. They stated that EBT removal depended on pH, temperature and contact time, and they achieved approximately 77% EBT removal from aqueous media even at low concentrations.

Single walled and multiwalled carbon nanotubes were prepared by Mamba et al. [50] and utilized for EBT photocatalytic degradation. They reported that single-walled carbon nanotubes incorporating photocatalyst displayed superior photocatalytic activity compared with the multiwalled carbon nanotubes incorporating counterpart. In addition, single-walled carbon nanotubes reached maximum degradation efficiencies of 89.2% for EBT [50]. Expanded perlite modified with orthophenanthroline was used as an adsorbent for the removal of EBT under various experimental parameters by Almeida et al. [17]. They obtained a removal efficiency of 100% at pH 3 for EBT and a minimal level of 28.50% EBT removal at alkaline pH. *Scolymus hispanicus* L. was used as an eco-friendly biosorbent to remove EBT from aqueous media [11]. They investigated various experimental conditions such as particle size, temperature, pH of solution, dye initial concentration, contact time and adsorbent dosage. The maximum biosorption amount of EBT was detected at pH 3. Based on equilibrium data including the Langmuir and Toth model, the best fit was obtained by the Toth model. The Langmuir model yielded a good fit to the experimental data with a maximum adsorption capacity which was obtained as 165.77 mg g^{-1} for EBT.

Tridax procumbens was made into activated carbon and prepared as an adsorbent by Raveendra et al. [16] for EBT removal. Various parameters such as contact time, adsorbent dosage, pH of solution and dye initial concentration were studied and optimized to evaluate their effect on EBT

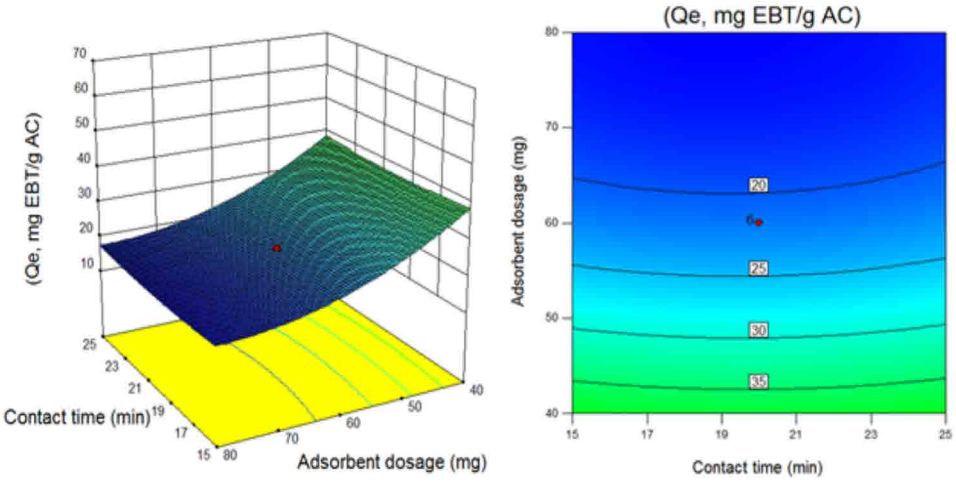


Fig. 7. Response surface and contour plot for EBT biosorption by AC as contact time and adsorbent dosage.

removal using activated carbon. The results of their studies revealed that using an adsorbent material is effective in removing azo dyes at low pH [16].

Aguila and Ligaray [2] prepared manganese oxide-coated zeolite to remove EBT from wastewater in a batch experiment process. They determined that the Freundlich model was the best for EBT adsorption on zeolite material. They gained an EBT removal percentage of 79.2% at 12 h. In another study, $NiFe_2O_4$ nanoparticles were synthesized and used to remove EBT from aqueous solutions. SEM, FTIR and XRD analysis and various experimental parameters were carried out and the adsorption capacity of the $NiFe_2O_4$ nanoparticles was obtained as 47.0 mg g^{-1} at pH 6.0 [4].

The present study was carried out using RSM with CCD model to optimize batch experimental studies for EBT removal from aqueous media. It was revealed that the maximum adsorption of EBT occurred at a pH of 6.5, temperature of 30°C, contact time of 20 min. and adsorbent dosage of 20 mg. AC biosorption capacity was calculated according to ANOVA and was determined as 64.2 mg EBT g^{-1} AC.

When it was compared with the studies in literature, AC was found to be efficiently utilized as an adsorbent at a rate higher than various nanoparticles, biosorbents and also activated carbon. Although various adsorbents have higher adsorption capacities for EBT than AC, they have various disadvantages including some being artificial and some causing problems for the environment as secondary pollutants. At the same time, the studies on EBT removal are usually carried out with kinetic models or percentages of elimination. There are a limited number of studies regarding the adsorption capacity of used adsorbent. The advantage of the present study is that AC is natural, environmentally friendly and was used as an adsorbent for EBT removal for the first time and showed high biosorption capacity for EBT.

4. Conclusion

This study aimed to remove EBT from aqueous medium by AC which is a low cost and naturally obtainable biosorbent. The removal of EBT was examined using CCD based on RSM. The results showed that the biomass of AC made it an ideal biosorbent for EBT. A statistical prediction method was successfully used to determine the combination effects of various factors such as adsorbent dosage, pH of solution, contact time and temperature. Under various examined conditions, the derived second-order polynomial model coefficient was obtained as 0.9967 which suggested that the experimental values were fitted well with the developed model. Under optimized conditions, an EBT removal rate of 100% from the aqueous solution was obtained. Solution pH, temperature and adsorbent dosage were found to be significant factors ($p < 0.01$) that influenced the removal of EBT by AC. When the solution temperature was increased and the adsorbent amount was decreased, the AC biosorption capacity increased. According to the present study; multi-parameter optimization with CCD was carried out and the following results were obtained:

- To reach a maximum EBT removal from aqueous media by AC, a CCD optimization procedure was performed. To find out a suitable model leading to optimum outcome conditions (pH: 6.5, temperature: 30°C, contact time: 20 min and adsorbent dosage: 20 mg), a CCD method was identified to yield a maximum EBT removal of 100%.
- The ANOVA results were satisfactory because of R^2 (0.9967) and Adj R^2 (0.9936) values. It can be said that 99.67% of the model-predicted values matched the experimental values for the adsorbed EBT by AC.
- The proposed mathematical model for EBT biosorption provided a critical analysis for the interactive influences of the selected independent variables'.
- The maximum AC biosorption capacity for EBT was found to be 64.2 mg EBT g^{-1} AC.
- To understand the relationship between the independent and response variables in addition to maximizing the process efficiency, the obtained results clearly confirmed that optimization is an effective approach for modeling the sorption process of EBT.

In conclusion, AC is an effective biosorbent for the removal of EBT from aqueous media and process factors remarkably influence EBT removal %. As a result, AC can be

used as an effective eco-friendly biosorbent for removal of other dyes.

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