Environment Protection Engineering

Vol. 44 2018 No. 2

DOI: 10.5277/epe180205

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EFFICIENCY OF RESPONSE SURFACE METHODOLOGY FOR OPTIMIZING REACTIVE BLUE 21 DYE REMOVAL WITH MODIFIED BENTONITE

Bentonite was modified with cetyltrimethylammonium bromide by a simple method and was used as an adsorbent for the removal of Reactive Blue 21 dye. Reactive Blue 21 is an important dye used in the textile industry, which is very harmful for living creatures, especially humans. The response surface methodology (RSM) was used to study the effect of independent variables such as dye concentration (20, 40, 60, 80 and 100 mg/dm^3), time (10, 20, 30, 40 and 50 min), initial pH (2, 4, 6, 8, 10) and modified bentonite dosage (1, 2, 3, 4 and 5 g/dm^3) on Reactive Blue 21 dye removal efficiency from aqueous solutions. At the optimum conditions (modified bentonite dosage 5 g/dm^3, dye concentration 61.3 mg/dm^3, pH 4.78; time14.31 min), the predicted removal of Reactive Blue 21 on modified bentonite was 93.22%. In a confirmatory experiment, 92.01% dye removal has been obtained. Thus, the experimental investigation and statistical approach enabled us to model adsorption of Reactive Blue 21 on modified bentonite.

1. INTRODUCTION

Many products in developed countries are colored in order to gain a beautiful appearance and general attraction acceptable by the consumers. Various dyes are used and it is possible to classify them based on chemical structure or methods of application [1]. The search for dyeing compounds that are capable of establishing a covalent bond with a fiber, chemically led to the production of reactive dyeing compounds. A general formula of reactive dyeing compounds is in the form of D-B-RG, in which D is usually the base of azo, anthraquinone, or phthalocyanine derivative [2]. Phthalocyanine reactive dyes are the most important dyes used in dyeing and textile industries. Phthalocyanine is an intensely blue-green-colored aromatic macrocyclic compound. Such dyes are often

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derivatives of copper phthalocyanine. They are toxic and dangerous even at low concentrations and are harmful to the health of living creature's especially human beings. Therefore, their removal from aquatic environments seems to be crucial [3].

Various methods such as membrane filtration, advanced oxidation [4], coagulation and precipitation [4], biological methods, and adsorption have been used to remove dye contaminants [5]. Adsorption of dye molecules on various adsorbents is a simple method of treatment. Various types of adsorbents include resins and carbonized polymers such as chitosan and its derivatives [6], firewood, polymer adsorbents, silica gel, activated alumina, clay, activated carbon such as pumice and walnut activated carbon [7], natural adsorbents, nanoadsorbents, bentonite and kaolin. Bentonite is a clay mineral and its major mineral is montmorillonite. Due to colloidal and malleable properties of bentonite, it is used in various industries. Bentonite $(Na)_{0.7}(Al_{3.3}Mg_{0.7})Si_8O_{20}(OH)_4 \times nH_2O$ is a fine grained clay which contains at least 85% of montmorillonite clay.

Clay, activated clay, and modified clay were used for removing Reactive Blue 21 (RB21) through adsorption from aquatic solutions. The results indicate economic significance of these materials as adsorbents [8]. Adsorption of Congo Red on bentonite and bentonite modified with cetyltrimethylammonium bromide (CTAB-MBn) revealed that CTAB-modified bentonite demonstrated high adsorption capacities toward acid dyes, while bentonite exhibited sorption capacities lower than CTAB-MBn [9]. The adsorption of Congo Red dye onto CTAB-kaolin was examined. The adsorption capacity of modified kaolin KC (24.46 mg/g) was found to be around 4 times higher than that of natural kaolin (5.94 mg/g). KC demonstrated the highest adsorption capacity by removing over 98% of CR after 10 min contact [10]. Removing dye from aquatic solutions using bentonite clay was studied along with the effect of various parameters. The results showed that bentonite clay is a suitable adsorbent for removing textile dye compounds from wastewaters [11].

The aim of this research was to modify bentonite using cetyltrimethylammonium bromide (B-CTAB) and investigate its efficiency in removing of Reactive Blue 21. In this regard, using an experimental design of the response surface methodology (RSM), evaluation of the effect of independent variables including contact time, dosage of adsorbent, dye concentration, and pH on the efficiency of B-CTAB in removing of Reactive Blue 21 was investigated.

Response surface methodology. RSM is a set of statistical techniques employed in optimization of processes where the intended response is influenced by a number of variables. Using this statistical model, the number of experiments decreased and all coefficients of the second-order regression model as well as the interactive effects of factors were estimated. By the RSM, the optimal state of factors was found and it indicates the way factors influence the results of experiments. The response is presented in the form of an integrated surface and a second-order polynomial is used for modeling of the response [2]. The second-order model is in the form of the following equation

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{1}$$

where, y is the predicted response, β_0 is a constant coefficient, β_i is the coefficient of linear effects, β_{ii} is the coefficient of squared effect, β_{ij} is the coefficient of interaction effects, X_i, X_j, X_iX_j are independent variables, and ε is a constant [12].

To identify the levels, codes such as (1), (0), and (–1) were used. This facilitates recording experimental conditions and experimental processes. The level of factors was chosen in a way that the top level is α, the lowest level is $-\alpha$, and the base level is 0. Central composite design is the most applicable design used in the RSM [12].

2. EXPERIMENTAL

The Reactive Blue 21 (molecular formula: $C_{40}H_{26}CuN_{10}O_{16}S_6$, molecular weight: 1159 g/mol) was purchased from Arta Tejarat Zarin Ardebil Co. Bentonite was prepared from Korea and cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were purchased from Merck Co., Germany.

Modification of bentonite. Modified bentonite was prepared by mixing 10 vol. % of bentonite and 10 g/dm^3 of CTAB which was added dropwise, and the solution was stirred for 3 h at ambient temperature. Thereafter, the precipitate was filtered and washed several times with distilled water. In order to obtain modified bentonite, it was dried in an oven at 105 °C for 3 h. The structural analysis of B-CTAB was taken by FTIR and XRD.

Analysis. To identify the prepared B-CTAB, FTIR (BRUKER-TENSOR 27, Germany) was employed along with a X-ray diffraction spectrophotometer device (XRD) (D5000, Siemens, Germany). In order to determine the concentration of the dye, UV-Vis spectrophotometer, DR5000-15V model, Hach Co. USA, was used (λ_{max} = 342 nm).

The percent dye removal R, amount of dye adsorbed (mg/g) at any time (q_t) and at equilibrium (q_e), were calculated from the following equations:

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \tag{2}$$

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{3}$$

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{4}$$

where, C_0, C_t and C_e are the initial, at any time, and equilibrium dye concentrations (mg/dm^3), respectively. V is the volume of the solution (dm^3) and M is the adsorbent weight (g).

Experimental design. To evaluate the effect of independent variables on the dye removal, a central composite design method was applied, using software Design-Expert 7 (DX7). The independent variables in this study included pH, contact time, initial concentration of dye, and dosage of adsorbent (Table 1). Using the RSM software, the operational data were fed into the software and 31 experiments were suggested (Table 2). To conduct the experiments, dye solutions were prepared with desired dye concentration, pH and dosage of adsorbent and stirred at the appropriate time. Thereafter, the samples were filtered and adsorption of samples of bentonite was determined using a UV-Vis spectrophotometer.

Table 1

Level variables for RB21 removing

Variable	$\alpha-$	–1	0	1	$\alpha+$
B-CTAB dosage, g/dm^3	1	2	3	4	5
Dye concentration, mg/dm^3	20	40	60	80	100
pH	2	4	6	8	10
Time, min	10	20	30	40	50

Table 2

Design of RSM and its experimental and predicted values

No.	B-CTAB dosage [g/dm^3]	[RB21] [mg/dm^3]	pH	Time [min]	Removal [%]		No.	B-CTAB dosage [g/dm^3]	[RB21] [mg/dm^3]	pH	Time [min]	Removal [%]	
					exp.	pred.						exp.	pred.
1	3	60	6	30	79.69	79.13	16	3	60	6	10	82.20	80.51
2	3	100	6	30	88.14	89.42	17	4	80	8	40	80.21	80.17
3	4	80	4	40	84.68	83.79	18	2	40	4	20	79.45	83.16
4	4	40	4	40	80.22	90.22	19	2	80	8	20	79.66	84.34
5	4	80	8	20	78.19	81.96	20	4	40	4	20	88.36	86.75
6	5	60	6	30	83.77	85.30	21	3	60	6	30	81.19	86.07
7	2	80	4	40	85.04	79.41	22	3	60	6	30	80.93	84.0
8	2	40	8	20	82.24	78.89	23	3	60	6	30	80.34	81.57
9	2	40	4	40	77.19	76.94	24	3	60	6	50	80.73	80.97
10	4	40	8	20	86.05	80.45	25	4	80	4	20	89.94	80.47
11	3	60	2	30	87.75	85.76	26	2	40	8	40	86.51	80.47
12	1	60	6	30	79.98	85.41	27	2	80	4	20	82.45	80.47
13	3	20	6	30	83.37	86.21	28	3	60	10	30	82.75	80.47
14	4	40	8	40	83.65	82.76	29	3	60	6	30	80.52	80.47

Isotherms. The isotherm equations revealed the adsorption properties that are crucial for designing the adsorption process [13]. Non-linear Langmuir and Freundlich isotherm models (Eqs. (5) and (6), respectively) were employed to evaluate the fitness of adsorption equilibrium data

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

$$q_e = K_F C_e^{1/n} \tag{6}$$

where, q_e is the amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg/g), C_e and $q_{\max}$ – dye equilibrium concentration (mg/dm^3) and the amount of dye adsorbed per unit mass of adsorbent for complete coverage with a single layer of adsorbate (mg/g), respectively. K_L is the adsorption equilibrium constant (dm^3/mg) of the Langmuir isotherm. K_F ((mg/g)·(mg/dm^{-3})$^{-1/n}$) and 1/n are the Freundlich isotherm constants [13].

3. RESULTS AND DISCUSSION

3.1. B-CTAB CHARACTERIZATION

Figure 1 shows the FTIR spectra of bentonite and B-CTAB. The characteristic peaks of bentonite within the range of 3432–3640 cm^{-1} correspond to the stretching vibrations of hydroxyl groups (ν_{OH}) which may have developed through isomorphic substitution in tetragonal and octagonal layers of bentonite [14].

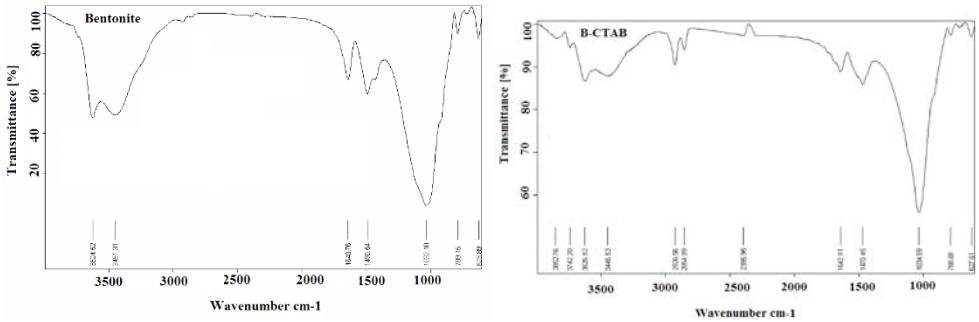

Fig. 1. FTIR of bentonite and B-CTAB

Peaks associated with aluminum, magnesium, and the limited number of water molecules present in the bentonite structure emerged within the range of 1640 cm^{-1}. The peak at 1032 cm^{-1} also belongs to the asymmetrical stretching vibration of Si–O–Si of bentonite. Furthermore, the peak at 789 cm^{-1} is one of the characteristic ones of quartz present in raw bentonite and the peak related at 623 cm^{-1} can be attributed to bending

vibrations of O–Si–O [15]. In the spectrum of bentonite modified with CTAB, a pair of peaks at 2850 cm^{-1} and 2900 cm^{-1} have emerged which are related to symmetrical and asymmetrical stretching vibrations of the methyl and methylene groups [8]. Alkaram et al. [13], also reached similar results in preparing bentonite modified with CTAB. Therefore, it can be concluded that the surface of bentonite has been well modified with surfactant.

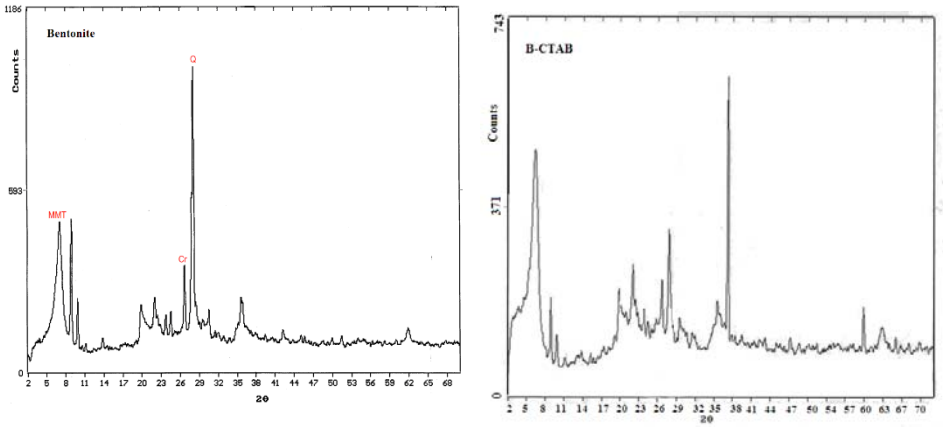

Fig. 2. XRD of bentonite and B-CTAB

Figure 2 shows the XRD patterns of bentonite and B-CTAB. Bentonite contains mainly montmorillonite ($2\theta = 7.05°$), crystallite ($2\theta = 26.71°$) and quartz ($2\theta = 28.12°$). The base distance (d) of montmorillonite is 12.52 Å, where the base distance of montmorillonite after modification with the surfactant has increased to 33.09 Å. This increase in the interlayer distance of bentonite shows the long chains of the surfactant within the interlayer space of montmorillonite occurred through cation exchange. Regarding bentonite modified with CTAB, it can be concluded the intensity of peaks implies introduction of CTAB surfactant in the bentonite structure. Therefore, FTIR and XRD results indicate that bentonite has been well modified with CTAB.

3.2. CONTACT TIME AND ADSORPTION ISOTHERMS

In order to find the time necessary to reach equilibrium, 60 mg/m^3 of dye solution was prepared and contacted with desired dose of B-CTAB. The adsorption process was carried out for 120 min, and every 5 min a sample was withdrawn from solution and its absorption was measured. It was found that the adsorption equilibrium was reached after 30 min (Fig. 3).

To determine the Langmuir and Freundlich isotherms, solutions of various initial concentrations of dye were prepared at pH 6.2 containing certain amounts of B-CTAB.

The results are shown in Fig. 4. The fitting of experimental and Freundlich results and high value of R^2 (Table 3) indicated the adsorption process of RB21 by B-CTAB follows the Freundlich isotherm model.

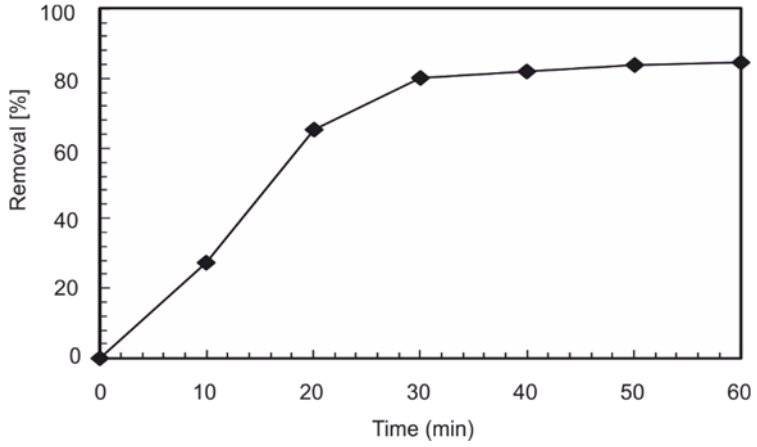

Fig. 3. Effect of contact time on Blue 21 removal
[B-CTAB] = 5 g/dm^3, [RB21] = 60 mg/dm^3, pH 6.2

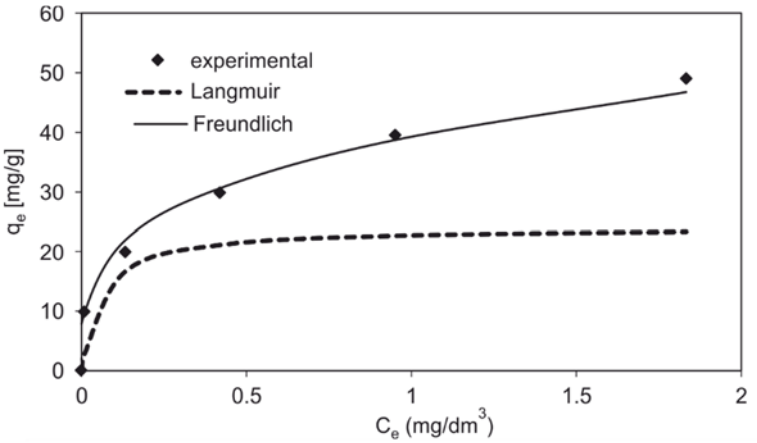

Fig. 4. Lagmuir and Freundlich isotherms for removal of RB21 with B-CTAB

Table 3

Isotherm parameters for adsorption of RB21 onto B-CTAB

Parameter	Langmuir			Freundlich		
	q_m [mg/g]	K_L [dm^3/mg]	R^2	$1/n$	K_F [dm^3/mg]	R^2
Value	22.87	1.83	0.897	0.33	5.54	0.987

3.3. RESPONSE AND VARIANCE (ANOVA) ANALYSES

The dependence of the degree of response (dependent variable) on the initial concentration of dye, the dosage of adsorbent, time, and pH (independent variables) was studied. The model in which the data was statistically calculated is a second order mathematical model. The equation obtained between the response (R) and each of the factors is as follows

$$\begin{aligned} Y = {} & 80.47 + 0.75X_1 + 0.60X_2 - 0.52X_3 - 0.14X_4 \\ & - 0.97X_1X_2 - 1.74X_1X_3 - 1.70X_1X_4 - 1.80X_2X_3 + 1.04X_2X_4 \\ & + 1.61X_3X_4 + 0.30X_1^2 + 1.27X_2^2 + 1.14X_3^2 + 0.20X_4^2 \end{aligned} \tag{7}$$

To analyze the responses and variables, the method of analysis of variance was used. In order to better understand the interaction of variables, three-dimensional plots were utilized. Table 4 presents the results of this analysis. In order to examine the validity of the obtained studies, the residual values (the difference between the experimental responses and predictive responses) were calculated.

Table 4

Analysis of variance (ANOVA) results for RB21 removal

Source	Sum of squares	Df	Mean square	F-value	P-value	Significance
Model	319.27	14	22.8	20.78	<0.0001	significant
X_1: dosage, g/dm^3	13.4	1	13.4	12.21	0.0033	
X_2: dye conc., mg/dm^3	8.7		8.7	7.93	0.013	
X_3: pH	6.39		6.39	5.83	0.029	
X_4: time, min	0.47		0.47	0.43	0.5205	
X_1X_2	14.91		14.91	13.59	0.0022	
X_1X_3	48.29		48.29	44.01	<0.0001	
X_1X_4	46.08		46.08	42	<0.0001	
X_2X_3	52.01		52.01	47.41	<0.0001	
X_2X_4	17.34		17.34	15.81	0.0012	
X_3X_4	41.37		41.37	37.71	<0.0001	
X_1^2	2.44		2.44	2.23	0.1565	
X_2^2	44.12		44.12	40.22	<0.0001	
X_3^2	35.76		35.76	32.6	<0.0001	
X_4^2	1.05		1.05	0.96	0.3439	
Residual	16.46	15	1.1			
Lack of fit	14.99	10	1.5	5.09	0.0432	not significant

$R^2 = 0.9510$, Adj-$R^2 = 0.9152$, adequate precision = 17.9.

3.5. EFFECT OF INDEPENDENT VARIABLES AND THEIR INTERACTION

Figure 5 shows three dimensional response surface plots of interaction between independent variables. Maximum dye removal was obtained for the maximum amount of adsorbent dose due to increase of contact surface area, whereas a low dye concentration corresponded to the greatest removal percentage (Fig. 5a). The reason for the dramatic decrease in the adsorption with the increase in initial concentration of the dye can be attributed to saturation of the active sites of the adsorbent and the reduction in the adsorption surface available [16].

In terms of the effect of pH and the dosage of adsorbent, the greatest removal value was obtained at 5 g/dm^3 of the adsorbent and pH 2 (Fig. 5b). Increase of pH resulted in a negative effect on the removal percentage of the dye. The maximum removal occurred in the acidic media. At pH below the ZPC, the surface has a positive charge while it has a negative charge at pH values above the ZPC. As calculated in this research, pH_{zpc} of B-CTAB solution was around 8 (not shown here), i.e., the surface of the adsorbent has a positive charge in the acidic media, while it has a negative charge in the alkaline media, according to the following reactions

$$SiOH + H^+ = SiOH_2^+ \tag{8}$$

$$SiOH + OH^- = SiO^- + H_2O \tag{9}$$

On the other hand, the RB21 will form with a species positively charged in acidic media by bonding a proton, and changes to a molecule with a negative charge in the alkaline media by losing it. Therefore, in the alkaline media, the repulsiveness of negatively charged surface of the adsorbent and the negatively charged surface of the dye (Reactive Blue 21 is an anionic dye) resulted in a decrease of dye adsorption onto B-CTAB. Thus, the greatest removal will take place in acidic solutions. Figure 5c demonstrates the interactive effect of dosage of adsorbent and time. The maximum removal occurred for the maximum amount of the adsorbent within ca. 15 min. In fact, during the initial stages of the adsorption, numerous active sites were available for adsorption of the dye. However, over time due to accumulation of dye molecules at the adsorption sites and development of a repulsion force between the molecules adsorbed onto the surface of solid and the molecules present in the solution phase, the adsorption decreases. The adsorbent becomes saturated and is no longer able to adsorb dye molecules [17]. As a result, the removal rate decreases upon increasing contact time.

The maximum removal occurred at the minimum concentration of the dye and low pH (Fig. 5d). These results agree with pervious findings on dye removal on bentonite. of The maximum removal of BR21 occurred in short time and low concentration (Fig. 5e). With respect to the interactive effect of pH and time, the maximum removal occurred at a low pH and within short periods of time (Fig. 5f).

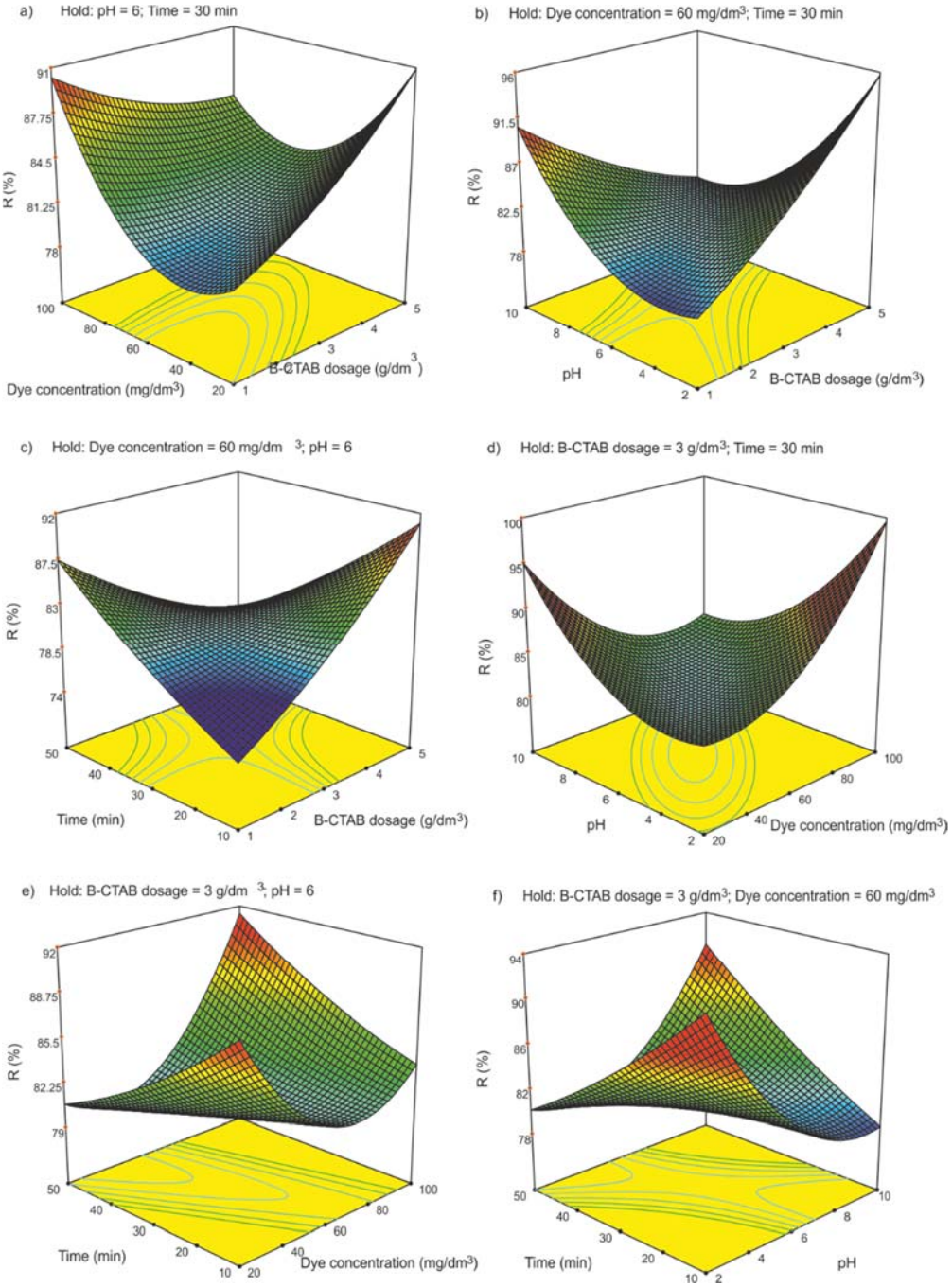

Fig. 5. Dependences of RB21 removal on: a) dye concentration and dosage, b) pH and dosage, c) time and dosage, d) pH and dye concentration, e) time and dye concentration, f) time and pH

Based on the statistical parameters (Table 4), the experimental methods along with the statistical analysis of the model (high value of $R^2 = 0.951$) suggest that dye removal can be defined using this model. Although, the value of $R^2_{adjusted}$ (0.915) is lower than the R^2 value, thus it can be deduced that the model has satisfactorily matched with the experimental data. The significance of the model for removing the dye was expressed through F-value = 20.78, where there is only a 0.01% chance that the F value is caused by noise.

The value of lack of fitting index, equal to 5.09, suggests that there is no significant relation between lack of fit and net error value and there is 4.32% probability that the lack of fit of the F prepared value is due to noise.

The Adeq precision value represents the difference between the model's predicted response and the mean value of the prediction error. If this ratio is larger than 4, then, it shows adequate distinction of the model. Therefore, the ratio of 17.9 of the second-order model proves removal of the dye. The proximity of the experimental and predicted values suggests the suitability of the designed model for removing RB 21 dye using B-CTAB.

3.6. OPTIMIZATION AND VALIDATION OF THE MODEL

Comparison of predicted and experimental R values indicates agreement between them and confirms that the model can be applied to predict of RB21 dye removal (Table 5).

Table 5

Optimum conditions obtained by RSE for removal of RB21

Experiment	Optimal conditions				R [%]		RSE
	X_1	X_2	X_3	X_4	Experimental	Predicted	[%]
1	0.25	35.2	7.31	12.9	91.34	93.13	1.27
2	0.25	61.3	4.78	14.31	92.01	93.22	1.62

Comparison of various adsorbents for the adsorption of RB21 is presented in Table 6. The results in the present study indicate that the B-CTAB can be an efficient adsorbent for removal of RB21 from aqueous solutions.

Table 6

Adsorption properties of various adsorbents towards RB21

Adsorbent	q_{max} [mg/g]	R [%]	Reference
Palm shell	24.7		[18]
Activated carbon	8.65		[19]
Nanoscale zero-valent iron		95	[20]

Table 6

Adsorption properties of various adsorbents towards RB21

Adsorbent	q_{max} [mg/g]	R [%]	Reference
Magnetic chitosan microparticles functionalized with polyamidoamine dendrimers	555.56		[21]
Seed residue of *Mabea fistulifera* Mart	11.13	85	[22]
Pomegranate residual-based activated carbon		98.7	[23]
Raw coal fly ash		33	[24]
Treated coal fly ash		88	
Tea waste	28.99	81	[25]
Natural wheat straw		68	[26]
Modified wheat straw		92.17	
Modified bentonite	22.87	92.01	this work

4. CONCLUSION

Bentonite modified with cetyltrimethylammonium bromide can effectively remove RB21 from aqueous solutions. The removal of RB21 using B-CTAB was about 89.94%, which is confirmed with the predicted removal value (80.47%). Therefore, the RSM may be used as a suitable model for removing RB21 dye using B-CTAB.

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