

## Desalination and Water Treatment

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tdwt20>

### Response surface methodological evaluation of the adsorption of textile dye onto biosilica/alginate nanobiocomposite: thermodynamic, kinetic, and isotherm studies

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Published online: 14 Aug 2014.

To cite this article: R. Darvishi Cheshmeh Soltani, A.R. Khataee, H. Godini, M. Safari, M.J. Ghanadzadeh & M.S. Rajaei (2014): Response surface methodological evaluation of the adsorption of textile dye onto biosilica/alginate nanobiocomposite: thermodynamic, kinetic, and isotherm studies, *Desalination and Water Treatment*, DOI: [10.1080/19443994.2014.950344](https://doi.org/10.1080/19443994.2014.950344)

To link to this article: <http://dx.doi.org/10.1080/19443994.2014.950344>

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## Response surface methodological evaluation of the adsorption of textile dye onto biosilica/alginate nanobiocomposite: thermodynamic, kinetic, and isotherm studies

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Received 23 April 2014; Accepted 7 July 2014

### ABSTRACT

The present investigation was carried out to synthesize biosilica/calcium alginate (CA) nanobiocomposite and evaluate the efficiency of as-prepared adsorbent for removing Direct Blue 71 (DB71) from aqueous solutions. Response surface methodology based on central composite design was applied to optimize the process. Accordingly, the maximum color removal of 81.49% was achieved at an initial DB71 concentration of 21 mg/L, adsorbent dosage of 2.4 g/L, contact time of 42 min and initial pH of 5. The negative values of Gibbs free energy ( $\Delta G^\circ$ ) and enthalpy change ( $\Delta H^\circ$ ), which were obtained during the thermodynamic study, revealed spontaneous and exothermic nature of the adsorption process, respectively. The adsorption of DB71 onto the nanobiocomposite followed pseudo-second-order kinetic model ( $R^2 = 0.977$ ) and Langmuir isotherm model ( $R^2 = 0.994$ ). The maximum adsorption capacity of biosilica/CA nanobiocomposite for the adsorption of DB71 was found to be 21.32 mg/g. The value of mean free energy (12.91 kJ/mol) indicated chemical adsorption of DB71 onto the adsorbent.

**Keywords:** Nano-siliceous adsorbent; Nanocomposite; Biocomposite; Adsorption; Experimental design

### 1. Introduction

Discharging colored effluents into aqueous environments such as rivers and lakes can cause

detrimental effects on aquatic life [1,2]. Among various chromogenic substances, azo dyes are the largest category discharged by various industries such as textile, food, paper, cosmetic, leather, and plastic [3,4]. Since azo dyes or their metabolites are toxic and potentially carcinogenic, the presence of organic azo

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dyes can cause threat to human health [3]. Therefore, the purification of colored effluents by several physical and chemical technologies has been considered [5–7]. Among different physicochemical technologies, the application of adsorption process has gained much more attention due to its simplicity, cost-efficiency, ease of operation, and low sensitivity to toxic environments [4–6,8–10]. In recent years, many researchers have focused on the use of locally available adsorbents such as clay minerals [11], agricultural wastes [12,13], and natural polymers [14] for removing organic dyes from aqueous solutions instead of expensive activated carbon. It has been reported that the silica-based materials can be used as efficient adsorbents due to the capability of their functional groups for sequestering target pollutants [15–17]. Thus, in the present study, the application of a siliceous adsorbent named biosilica was considered for treating colored solutions. Biosilica is a biological sedimentary rock composed of nearly 90% silica, which is suitable for the adsorption of organic dyes because of its high surface area containing surficial functional groups [4]. However, it is difficult to withdraw and recover fine biosilica particles after the adsorption for subsequent utilization. Therefore, the immobilization of biosilica within a suitable material was taken into account to avoid releasing the particles into the environments and make the process cost-efficient. In addition, the immobilization of fine adsorbents is an essential step for full-scale applications [4,8,18]. Many polymeric substances such as alginate [8,19,20], chitosan [18,20], polyethyleneimine [21], carboxy methyl cellulose [20], and polyvinyl alcohol [20,22] have been applied for the entrapment of different fine adsorbents. Alginate, as a natural carbohydrate polymer derived from brown algae, has been widely employed for the immobilization of various adsorbents because of its biodegradability, hydrophilicity, mechanical stability, and ease of preparation [3,8]. Moreover, high potential of the alginate matrix for the adsorption of organic dyes has been demonstrated [19,23]. Therefore, the utilization of alginate can be an efficient alternative for the immobilization of fine adsorbents such as biosilica. Hence, in the present study, biosilica particles were incorporated into the alginate matrix and used as adsorbent for the removal of an azo dye (Direct Blue 71 (DB71)) from aqueous solutions. The toxicity of direct dyes to living organisms such as *Daphnia magna* has been demonstrated [24,25]. To the best of our knowledge, there is no report on the use of immobilized biosilica within calcium alginate (CA) for the adsorption of organic dyes in aqueous phase. To evaluate the effect of various operational parameters, response surface methodology (RSM) based on central composite design (CCD)

was applied as statistical approach. Reduced number of experimental runs, capability to evaluate the interactive effects of the operational parameters, and possibility to optimize the operational parameters for achieving maximum efficiency are the advantages of RSM approach in comparison with the conventional one-factor-at-a-time statistical strategy [26–30]. In the next step, thermodynamic, kinetic, and isotherm studies were carried out to reach a better understanding of the adsorption process designed for the removal of DB71.

## 2. Materials and methods

### 2.1. Chemicals

Direct blue 71 (an anionic azo dye with molecular formula:  $C_{40}H_{23}N_7Na_4O_{13}S_4$  and molecular weight: 1029.87 g/mol) was purchased from Nasaj Sabet Company, Iran, and used without any purification. Nano-sized biosilica (molecular weight of 1.495 g/mol, and  $SiO_2$  basis >95%), which was of analytical grade, was purchased from Sigma-Aldrich, USA. Sodium alginate from *Laminaria hyperborean* was purchased from BDH Laboratory Supplies (Poole, England) and used for the immobilization of biosilica particles. All other reagents and chemicals were of analytical grade and were obtained from Merck, Germany. The pH of solutions was adjusted using 0.1 M NaOH or 0.1 M HCl.

### 2.2. Preparation of biosilica/CA nanobiocomposite

To immobilize the adsorbent, 20 g of nano-sized biosilica was mixed in 500 mL of 2% sodium alginate solution. The mixture was magnetically stirred for 1 h at 100 rpm to reach a homogeneous mixture and was kept for a day to obtain a bubble-free blend. The resulted compound was added dropwise via a syringe to 1 L of 0.5 M calcium chloride solution. Calcium atoms can create salt bridges between the  $\alpha$ -L-guluronic acids (G) blocks of alginate matrix to form CA. As a result of above-mentioned reactions, the immobilized adsorbent was in bead form. After keeping the beads in calcium chloride for 24 h, the beads were withdrawn from the solution and washed with deionized water to remove impurities. Then, they were dried at room temperature until achieving actual size [8]. Finally, the beads were ground and sieved using standard sieves. The size distribution of applied beads was between 10 and 20 mesh.

### 2.3. Experimental proceedings and design

Batch experimental runs were carried out using 100-mL Erlenmeyer flasks. These flasks were placed

on a shaker and thoroughly stirred. Additionally, a shaker incubator (Model: ISH 554D, Fannavarane Sahand Azar, Iran) was applied for conducting thermodynamic study. CCD model was used to evaluate the effect of four main operational parameters influencing the adsorption of DB71 onto biosilica/CA nanobiocomposite, including initial DB71 concentration (mg/L), adsorbent dosage (g/L), contact time (min), and initial pH. The number of experimental runs was calculated via Eq. (1):

$$N = 2^k + 2k + x_0 \quad (1)$$

where  $N$ ,  $k$ , and  $x_0$  are the number of experiments, the number of operational parameters, and the number of replications as central points, respectively [31]. According to the aforementioned equation, the total number of experimental runs was obtained to be 31 ( $k = 4$ ,  $x_0 = 7$ ). An empirical second-order polynomial equation was employed to describe the relationship between the dependent parameter (color removal (%)) and the studied operational parameters as shown in Eq. (2):

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \left( \sum_{i=1}^n b_{ii} x_i \right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \quad (2)$$

where  $Y$  is the predicted color removal (%) and  $b_0$ ,  $b_i$ ,  $b_{ij}$ , and  $b_{ii}$  are constant, linear, interaction, and quadratic coefficients, respectively. In addition,  $x_i$  and  $x_j$  are the coded values for the experimental parameters [27,29,32,33]. The experimental ranges and levels of the operational parameters concerning color removal are tabulated in Table 1. The ranges and levels of the operational parameters were selected based on the results of preliminary experiments.

#### 2.4. Analytical procedure

Morphological structure of the biosilica/CA nanobiocomposite was analyzed via scanning electron

microscopy (SEM) by means of a TESCAN microscope (Model: MIRA3, Czech Republic). In addition, Fourier transform infra-red (FT-IR) analysis was conducted using an infra-red spectrophotometer (Tensor 27, Bruker, Germany) in the wavenumber ranging from 400 to 4,000  $\text{cm}^{-1}$  to assess the role of functional groups of the nanobiocomposite in the adsorption of DB71. For the measurement of residual DB71 concentration, the sample was taken out and centrifuged for 5 min at 5,000/min. Then, it was spectrophotometrically measured with a Hach UV-vis spectrophotometer (DR 5000, USA) at maximum wavelength of 577 nm.

### 3. Results and discussion

#### 3.1. SEM and FT-IR analysis

To evaluate surface morphology of the biosilica/CA nanobiocomposite, SEM analysis was conducted and the results are depicted in Fig. 1. A rugged, uneven and porous surface for the nanobiocomposite can be observed in Fig. 1((a)–(d)), which is appropriate for the adsorption of target pollutant in aqueous phase. The results of our previous study indicated that biosilica is composed of nano-sized crystals (20 nm) and nano-porous structure with pore diameter size distribution ranging from 60 to 70 nm [4]. Furthermore, as can be obviously seen from Fig. 1((b)–(d)), the immobilization of nano-sized biosilica particles by CA has been performed appropriately. The presence of nano-sized biosilica adjacent to the CA is evidently shown in Fig. 1(b). As can be observed in Fig. 1(c), the immobilization of nano-sized biosilica within CA resulted in the formation of nanostructured beads on the surface of entrapped biosilica, which creates a suitable surface area for the adsorption process. In the following, FT-IR analysis was conducted to determine the role of various surficial functional groups on the adsorption of DB71. The presence of some main functional groups on the surface of biosilica/CA nanobiocomposite is evident in Fig. 2. As shown, the peaks centered at 3,400  $\text{cm}^{-1}$  (corresponding to the stretching vibration of –OH, amino, and amide groups and their

Table 1  
Ranges and levels of the experimental parameters for the adsorption of DB71 onto biosilica/CA nanobiocomposite

Run no.	Code	Parameter	Parameter level				
			–2 ( $\alpha$ )	–1	0	+1	+2 ( $\alpha$ )
1	$X_1$	Dye concentration (mg/L)	10	20	30	40	50
2	$X_2$	Adsorbent dosage (g/L)	0.5	1.0	1.5	2.0	2.5
3	$X_3$	Reaction time (min)	5	20	35	50	65
4	$X_4$	Initial pH	3	5	7	9	11



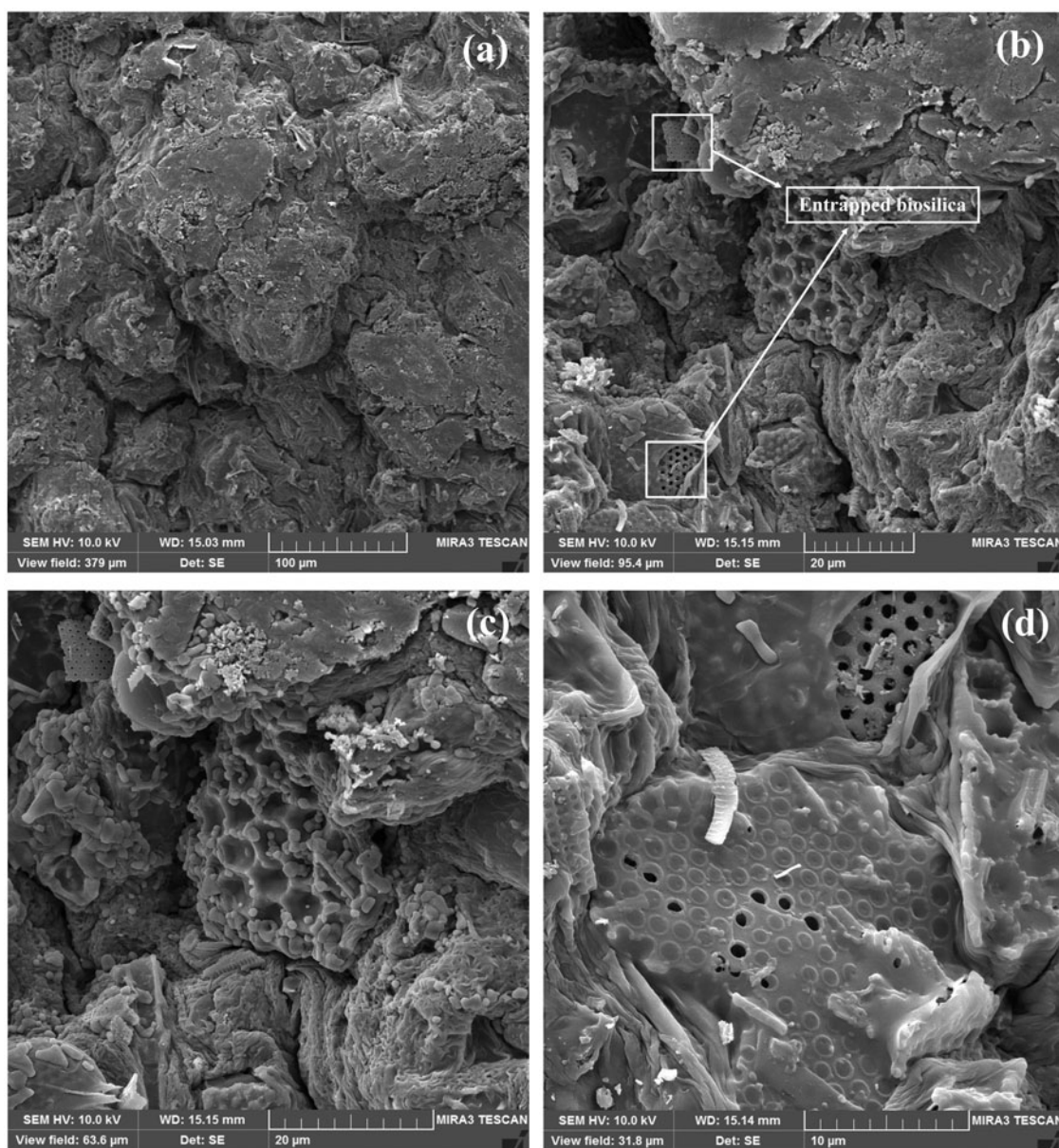


Fig. 1. SEM images of biosilica/CA nanobiocomposite at different magnifications ((a)–(d)).

overlapping) [14,23,34],  $2,926\text{ cm}^{-1}$  ( $-\text{CH}$  band) [35],  $1,641\text{ cm}^{-1}$  ( $-\text{OH}$  bending mode of adsorbed  $\text{H}_2\text{O}$ ) [16],  $1,762\text{ cm}^{-1}$  (stretching vibration of  $\text{C}=\text{O}$  from the carboxylic groups) [36],  $1,454\text{ cm}^{-1}$  ( $-\text{CH}$  bending of alkene (in plane)) [4],  $1,261\text{ cm}^{-1}$  (stretching vibrations of  $-\text{CH}$  bonds) [15],  $1,050\text{ cm}^{-1}$  ( $\text{Si}-\text{O}-\text{Si}$  stretching) [37],  $861\text{ cm}^{-1}$  (symmetric stretching of  $\text{Si}-\text{O}-\text{Si}$ ) [38],  $782\text{ cm}^{-1}$  ( $\text{Si}-\text{O}$  (out-of-plane) band) [39], and  $480$  (the  $\text{Si}-\text{O}-\text{Si}$  bond of condensed silica network) [16] were diminished after the adsorption of DB71, indicating that major portion of the functional groups placed on

the surface of biosilica/CA nanobiocomposite are involved in the adsorption of DB71.

### 3.2. CCD results for decolorization of the dye

CCD model is one of the most widely applied statistical methods for the optimization of different operational parameters influencing the efficiency of experimental reactors [27,28,40–42]. Using CCD model, a second-order polynomial quadratic equation was obtained to describe mutual relationship between

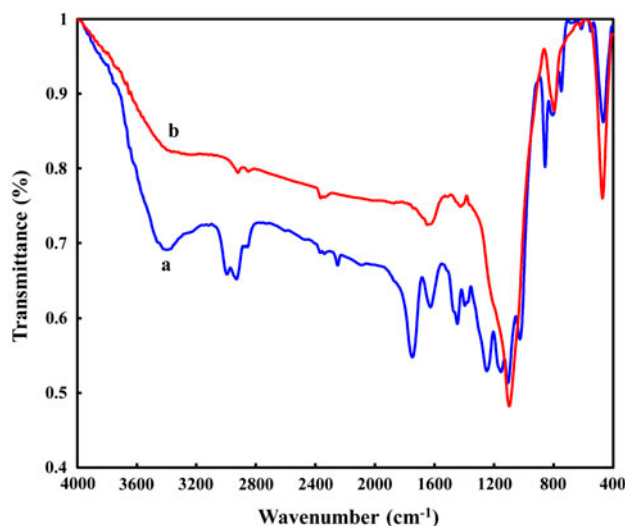


Fig. 2. FT-IR spectra of biosilica/CA nanobiocomposite before (a) and after (b) the adsorption of DB71.

different operational parameters (DB71 concentration ( $x_1$ ), adsorbent dosage ( $x_2$ ), contact time ( $x_3$ ), and initial pH ( $x_4$ )) and specified response (color removal (%)), which is exhibited in Eq. (3):

$$Y(\text{CR}(\%)) = 64.32 - 12.88x_1 + 6.21x_2 + 8.00x_3 - 3.94x_4 + 1.15x_1x_2 + 0.42x_1x_3 + 0.052x_1x_4 - 1.23x_2x_3 - 0.77x_2x_4 - 0.084x_3x_4 - 2.16x_1^2 - 2.68x_2^2 - 1.68x_3^2 - 1.61x_4^2 \quad (3)$$

The prediction of color removal (%) under different values of the operational parameters within the specified ranges can be achieved through Eq. (3). Based on Eq. (3), the experimental conditions (coded and actual parameters) together with experimental and predicted CR (%) are shown in Table 2. To assess significance of the CCD model for predicting the adsorption of DB71 onto biosilica/CA nanobiocomposite, analysis of variance (ANOVA) was performed [32,40,42]. The results of ANOVA are given in Table 3. The significance of the model can be checked by the correlation coefficients obtained via ANOVA [29]. The correlation coefficient was obtained using Eq. (4):

$$R^2 = 1 - (SS_{\text{residual}} / SS_{\text{model}} - SS_{\text{residual}}) \quad (4)$$

where  $SS$  is the sum of square [43]. According to the data given in Table 3, a high correlation coefficient ( $R^2 = 0.953$ ) between the predicted and experimental

CR (%) was obtained, which indicated that the applied model can be reliable for predicting CR (%). The plot of predicted CR (%) vs. experimental CR (%) is depicted in Fig. 3(a), exhibiting good agreement between the predicted and experimental CR (%). The correlation coefficient of 0.953 demonstrated that 95.3% of the variations for CR (%) are explained by the model, but the model does not explain 4.7% of the variations of CR (%) [44]. In addition, the value of adjusted  $R^2$  adjusts the value of  $R^2$  regarding the sample size and the number of operational parameters and statistical terms based on the degrees of freedom [29,45]. From the other point of view, adjusted  $R^2$  modifies  $R^2$  by taking into consideration the number of covariates in the model. The value of adjusted  $R^2$  for the adsorption of DB71 onto biosilica/CA nanobiocomposite was calculated through Eq. (5):

$$\text{Adjusted } R^2 = 1 - ((n - 1)/(n - p)(1 - R^2)) \quad (5)$$

where  $n$  and  $p$  are the number of experimental runs and predictors in the CCD model, respectively [43]. The obtained value for adjusted  $R^2$  (0.913) was close to the value of  $R^2$  (0.953), suggesting a good fitness between the predicted and experimental CR (%). As can be seen from Table 3, the high value of adequate precision (18.94) and low value obtained for the coefficient of variation ( $CV = 8.12\%$ ) indicated suitability of the applied model for the prediction of CR (%) under different experimental conditions. The preferred value for “adequate precision” is greater than 4 [28]. Residuals, which can be obtained through calculation of the difference between the experimental and predicted CR (%), exhibit how well the applied model satisfies the assumptions of ANOVA [42,45]. The plots of residuals vs. run number, predicted CR (%), and experimental CR (%) were depicted in Fig. 3(b–d), respectively. As illustrated, the residuals towards run number, predicted CR (%), and experimental CR (%) are randomly distributed, implying normal distribution of the residuals. One of the approaches, which can be used for the evaluation of the importance of individual and interactive effects of the operational parameters, is the comparison of  $F$ - and  $p$ -values obtained for each model term. The larger the quantity of the  $F$ -values and smaller  $p$ -values, the more meaningful is the corresponding coefficient estimate [42,44]. Among individual effects, the initial DB71 concentration ( $x_1$ ) with  $F$ -value of 179.5 and  $p$ -value of 0.0001 produces the largest effect on CR (%), while the initial pH ( $x_4$ ) with  $F$ -value of 16.79 and  $p$ -value of 0.0008 produced the lowest individual effect on CR (%). As given in

Table 2

Experimental and predicted results for the adsorption of DB71 onto biosilica/CA nanobiocomposite

Run no.	Coded parameters				Actual parameters				Color removal (%)	
	$X_1$	$X_2$	$X_3$	$X_4$	$X_1$	$X_2$	$X_3$	$X_4$	Experimental CR (%)	Predicted CR (%)
1	+1	+1	+2	+1	40	2.0	50	9	52.33	53.12
2	0	0	0	-1	30	1.5	35	3	69.23	65.76
3	+1	+1	-1	-2	40	2.0	20	5	47.23	48.06
4	0	+2	0	0	30	2.5	35	7	73.12	66.04
5	0	0	0	0	30	1.5	35	7	62.08	64.32
6	0	0	0	0	30	1.5	35	7	65.79	64.32
7	+1	-1	+1	+1	40	1.0	50	9	43.21	42.38
8	0	0	0	0	30	1.5	35	7	69.49	64.32
9	0	0	0	+2	30	1.5	35	11	46.04	50.01
10	-1	-1	-1	-1	20	1.0	20	5	60.02	58.34
11	-1	-1	+1	+1	20	1.0	50	9	71.22	69.50
12	+1	+1	+1	-1	40	2.0	50	5	58.11	62.60
13	+1	-1	-1	+1	40	1.0	20	5	31.49	29.34
14	+1	-1	+1	-1	40	1.0	50	5	47.65	48.79
15	-1	+1	+1	-1	20	2.0	50	5	81.32	85.33
16	-1	-1	-1	+1	20	1.0	20	9	56.16	52.06
17	0	-2	0	0	30	0.5	35	7	33.61	41.19
18	0	0	0	0	30	1.5	35	7	63.45	64.32
19	+1	-1	-1	+1	40	1.0	20	9	28.17	23.27
20	0	0	0	0	30	1.5	35	7	66.45	64.32
21	+1	+1	-1	+1	40	2.0	20	9	37.11	38.92
22	+1	+1	-1	+1	20	2.0	20	9	65.13	63.10
23	0	0	0	0	30	1.5	35	7	60.11	64.32
24	+1	0	0	0	50	1.5	35	7	30.74	29.90
25	0	0	-1	0	30	1.5	5	7	36.35	41.60
26	-1	+1	+1	+1	20	2.0	50	9	73.11	75.64
27	-1	-1	+1	-2	20	1.0	50	5	77.54	76.12
28	-1	+1	-1	-1	20	2.0	20	5	71.23	72.45
29	0	0	+2	0	30	1.5	65	7	78.33	73.58
30	0	0	0	0	30	1.5	35	7	62.87	64.32
31	-2	0	0	0	10	1.5	35	7	80.08	81.42

Table 3

The results of ANOVA for the adsorption of DB71 onto biosilica/CA nanobiocomposite

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value	
Regression	7,254.10	14	518.15	23.36	0.0001	Significant
Residuals	354.85	16	22.18			
Lack of fit	295.85	10	29.59	3.01	0.0953	Not significant
Pure error	59.03	6	9.84			
Total	7,608.98	30				

Notes:  $R^2 = 0.953$ , adjusted  $R^2 = 0.913$ , adequate precision = 18.94, coefficient of variation (CV) = 8.12 (%).

Table 4, the interactive effects ( $x_{12}$  with  $F$ -value of 0.96,  $x_{13}$  with  $F$ -value of 0.12,  $x_{14}$  with  $F$ -value of 0.002,  $x_{23}$  with  $F$ -value of 1.08,  $x_{24}$  with  $F$ -value of 0.42 and  $x_{34}$  with  $F$ -value of 0.005) produced lower effects on CR (%) in comparison with individual effects.

Obviously, the interactive effect of adsorbent dosage and contact time ( $x_{23}$ ) caused the greatest interactive effects, while the interactive effect of initial DB71 concentration and initial pH ( $x_{14}$ ) caused the lowest interactive effects.

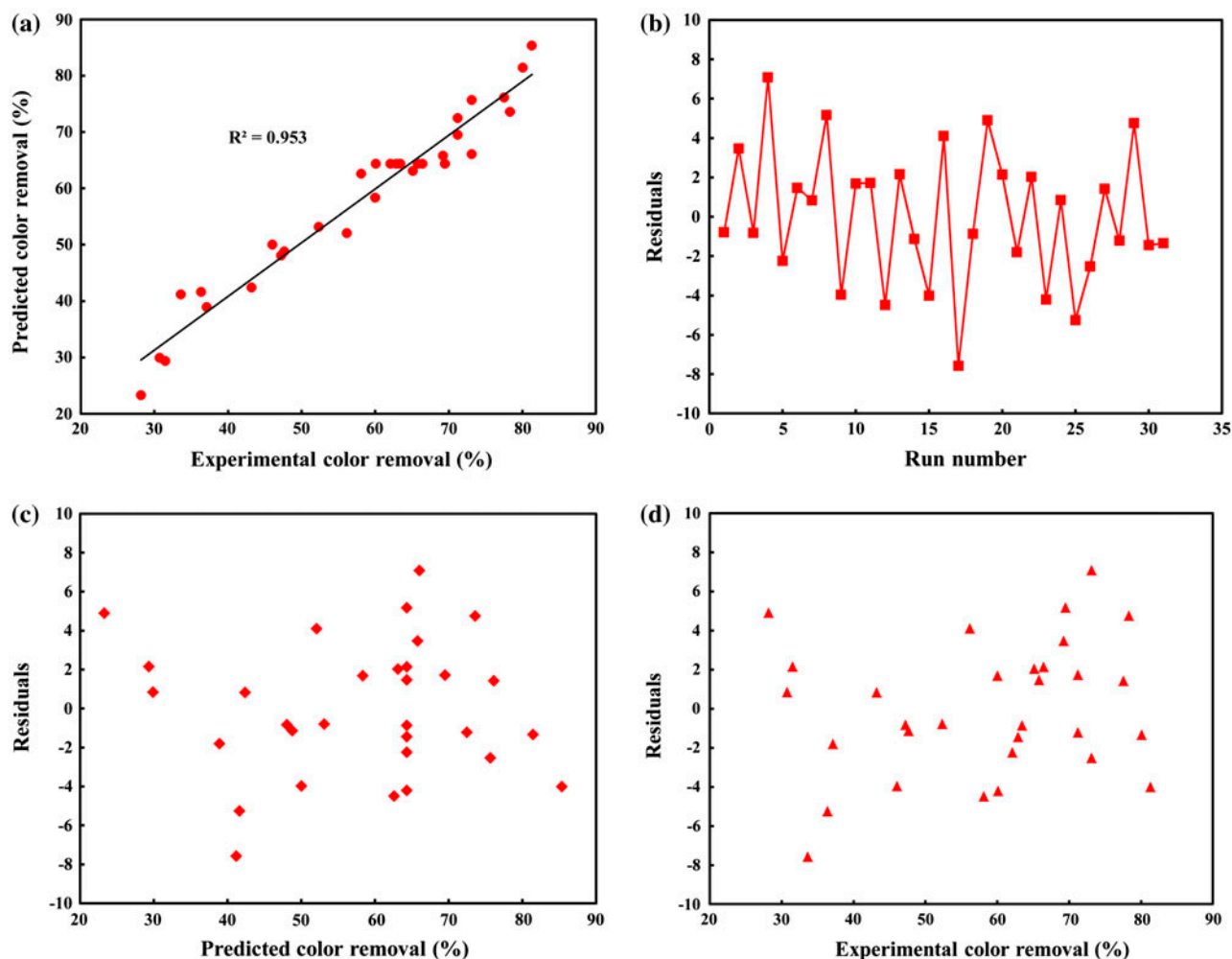


Fig. 3. Predicted color removal vs. experimental color removal (a) and together with corresponding residual plots ((b)–(d)).

### 3.3. The effect of operational parameters

Response surface plots and corresponding contour plots were employed to study the interactive effects of various operational parameters on the adsorption of DB71 from aqueous phase. The response surface plots (3-D) of the response as a function of two independent parameters can be beneficial in understanding the interactive effects of selected independent parameters [29]. Fig. 4(a) and (b) shows the effect of initial DB71 concentration on CR (%), where the adsorbent dosage and initial pH were constant at 1.5 g/L and 7, respectively. As shown, increasing initial DB71 concentration from 10 to 50 mg/L resulted in decreasing CR (%) within contact time of 65 min. At lower initial dye concentrations, all dye molecules will be adsorbed onto adsorptive sites, resulting in higher CR (%). The lower CR (%) at higher dye concentrations can be due to the saturation of adsorptive sites of the

nanobiocomposite [19]. Similar result has been reported by Chen and Lin in the adsorption of Reactive red 22 by immobilized biomass in alginate–silicate sol–gel beads [3]. Fig. 5(a) and (b) exhibited that how increasing adsorbent dosage and contact time led to increasing CR (%), where the initial DB71 concentration and initial pH were constant at 30 mg/L and 7, respectively. Increasing CR (%) with adsorbent dosage can be ascribed to the increased adsorbent surface and adsorptive sites for sequestering dye molecules in aqueous phase [23,46]. As shown in Fig. 6(a) and (b), the CR (%) was gradually increased with decreasing initial pH along with increasing contact time. In this set of experiments, the initial DB71 concentration and adsorbent dosage were constant at 30 mg/L and 1.5 g/L, respectively. Enhanced adsorption of DB71 by the nanobiocomposite at acidic pH values can be attributed to the protonation of the surface of



Table 4

Estimated regression coefficient and corresponding  $F$ - and  $p$ -values obtained during CCD for the adsorption of DB71 onto biosilica/CA nanobiocomposite

Coefficient	Coefficient estimate	Standard error	$F$ -value	$p$ -value
$x_0$	64.32	1.78	23.36	0.0001
$x_1$	-12.88	0.96	179.5	0.0001
$x_2$	6.21	0.96	41.78	0.0001
$x_3$	8.00	0.96	69.19	0.0001
$x_4$	-3.94	0.96	16.79	0.0008
$x_{12}$	1.15	1.18	0.960	0.3440
$x_{13}$	0.42	1.18	0.120	0.7287
$x_{14}$	0.052	1.18	0.002	0.9654
$x_{23}$	-1.23	1.18	1.080	0.3134
$x_{24}$	-0.77	1.18	0.420	0.5241
$x_{34}$	-0.084	1.18	0.005	0.9438
$x_{11}$	-2.16	0.88	6.040	0.0258
$x_{22}$	-2.68	0.88	9.230	0.0078
$x_{33}$	-1.68	0.88	3.650	0.0742
$x_{44}$	-1.61	0.88	3.340	0.0865

adsorbent and subsequently electrostatic attraction between negatively charged anionic dye and positively charged surface of the nanobiocomposite [47], while increasing initial pH resulted in increasing the number of negatively charged sites on the surface of the nanobiocomposite leading to the electrostatic repulsion between anionic dye molecules and negatively charged sites on the surface of the adsorbent [14]. Three-dimensional surface plot (Fig. 6(a)) and corresponding contour plot (Fig. 6(b)) of the effect of initial pH indicated a little increment in the CR (%) with decreasing initial pH.

### 3.4. Numerical optimization of decolorization process

To reach optimized values of the operational parameters for the maximum CR (%), numerical optimization was applied in which the CR (%) as response was set to "maximize" and the operational parameters were set to "in range." The result of numerical optimization showed that a maximized CR (%) of 81.49% can be achievable with initial DB71 concentration of 21 mg/L, adsorbent dosage of 2.4 g/L, contact time of 42 min, and initial pH of 5. Additionally, confirmatory experiments were performed under optimized values to verify the result of numerical optimization. As result, a mean value of  $84.06 \pm 3.58\%$  was obtained for CR (%) during the confirmatory experiments under optimum operational parameters, indicating the reliability of applied model for the estimation of real conditions.

### 3.5. Thermodynamic study

The thermodynamic study was accomplished via changing the solution temperature between 293 and 313 K according to the "0" level of the range of studied operational parameters (DB71 concentration of 30 mg/L, adsorbent dosage of 1.5 g/L and initial pH of 7) within contact time of 60 min. The Gibbs free energy ( $\Delta G^\circ$ ) (kJ/mol), entropy change ( $\Delta S^\circ$ ) (kJ/mol K), and enthalpy change ( $\Delta H^\circ$ ) (kJ/mol) for the adsorption of DB71 onto biosilica/CA nanobiocomposite were estimated via Eqs. (6) and (7):

$$\Delta G^\circ = -RT \ln K_D \quad (6)$$

$$\ln K_D = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \quad (7)$$

where  $T$  (K),  $K_D$  ( $q_e/C_e$ ), and  $R$  are the temperature of solution, distribution coefficient, and the universal gas constant, respectively [39,48,49]. The value of  $\Delta H^\circ$  and  $\Delta S^\circ$  were gained through the slope ( $-\Delta H^\circ/R$ ) and intercept ( $\Delta S^\circ/R$ ) of the plot of  $\ln K_D$  vs.  $1/T$ . The values of thermodynamic parameters are listed in Table 5. As shown, the obtained negative values for  $\Delta G^\circ$  and  $\Delta H^\circ$  demonstrated spontaneous and exothermic nature of the adsorption of DB71 onto the nanobiocomposite. The high value of  $\Delta H^\circ$  showed a moderately strong binding between the adsorbed DB71 and the surficial functional groups of the nanobiocomposite. Besides, the negative value of  $\Delta S^\circ$  implies lower degree of freedom of adsorbed DB71 and subsequently strong

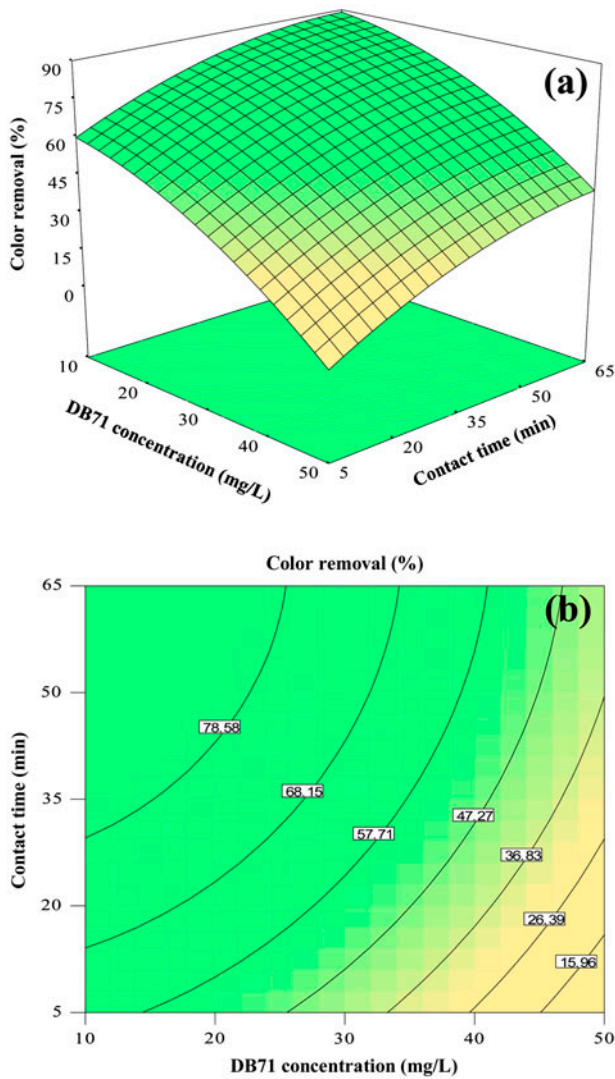


Fig. 4. Three-dimensional plot (a) and corresponding contour plot (b) for interactive effect of initial dye concentration and reaction time.

attraction between the adsorbate molecules and surficial functional groups of the nanobiocomposite [50].

### 3.6. Kinetic study

Predicting the rate of adsorption process is one of the most important factors during designing adsorption systems to be used in full-scale applications [46]. The pseudo-first- and pseudo-second-order kinetic models were employed to reach a better understanding of the mechanism of DB71 removal through the adsorption onto biosilica/CA nanobiocomposite. The kinetic study was carried out at an initial DB71 concentration of 30 mg/L, adsorbent dosage of 1.5 g/L,

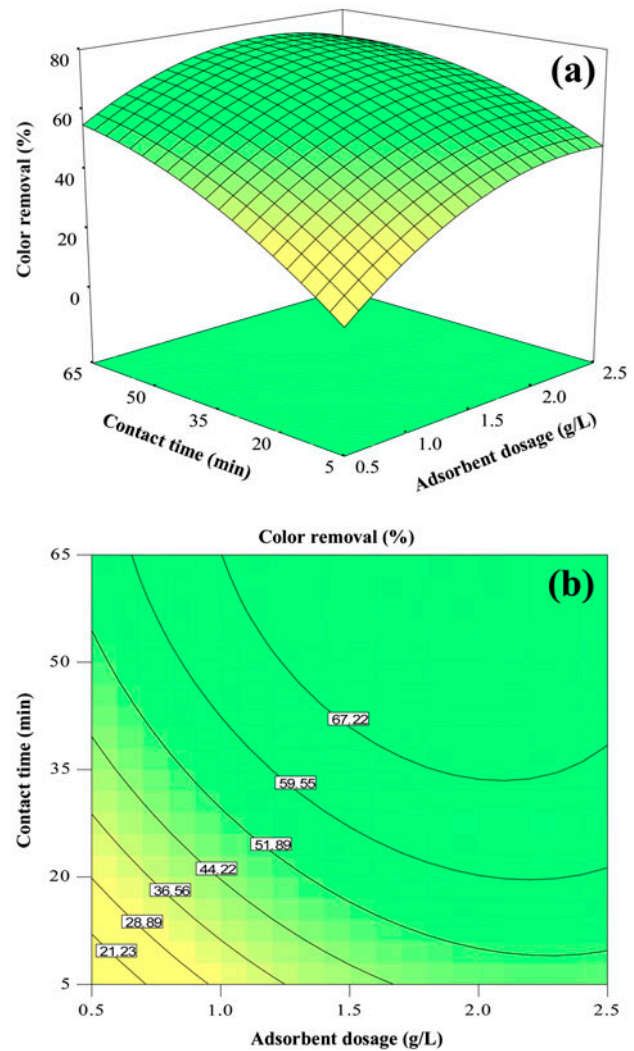


Fig. 5. Three-dimensional plot (a) and corresponding contour plot (b) for interactive effect of adsorbent dosage and reaction time.

and initial pH of 7 within contact time of 60 min. The adsorption of DB71 onto biosilica/CA nanobiocomposite reached equilibrium within 60 min and further increase in contact time did not significantly increase the amount of adsorbed dye (data not shown). The linear form of the pseudo-first-order kinetic model is shown through Eq. (8):

$$\log(q_e - q_t) = \log q_e - (k_{1,ads}/2.303)t \quad (8)$$

where  $q_t$  and  $k_{1,ads}$  are the amount of adsorbed DB71 at time  $t$  (mg/g) and the rate constant (1/min), respectively [51]. To depict the linear regression of the pseudo-first-order model,  $\log(q_e - q_t)$  was plotted vs.  $t$ . Based on the equation of linear regression, kinetic

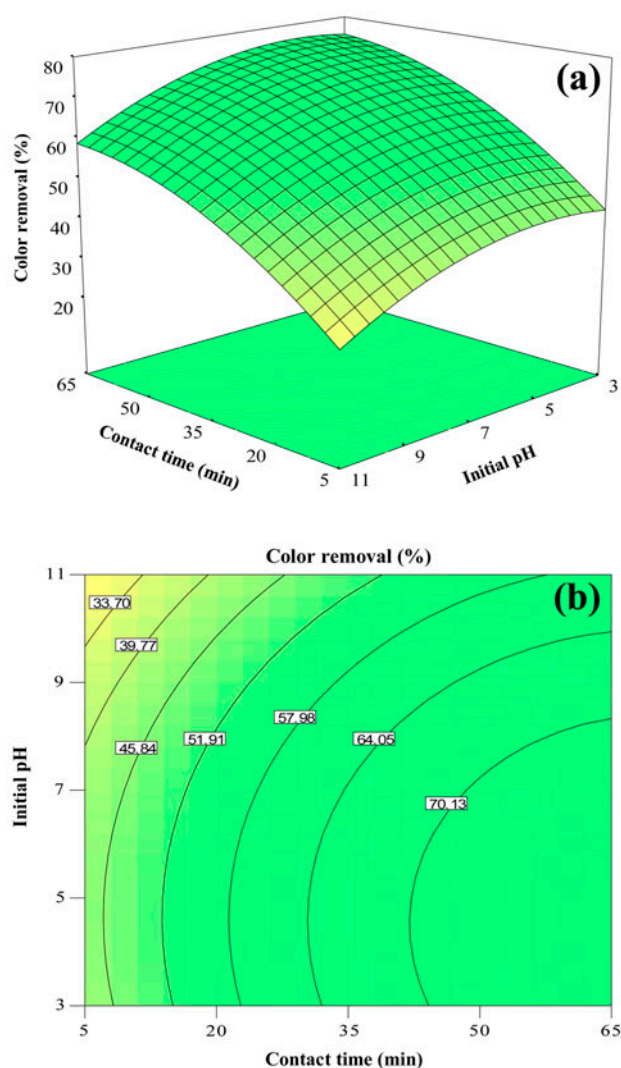


Fig. 6. Three-dimensional plot (a) and corresponding contour plot (b) for interactive effect of initial pH and reaction time.

parameters corresponding to the pseudo-first-order model were determined. The intercept and slope of the plot determine the values of  $q_e$  and  $k_{1,ad}$ , respectively. In addition, the linear form of the pseudo-second-order kinetic model is displayed in Eq. (9):

$$t/q_t = (1/k_{2,ad}q_e^2) + (1/q_e)t \quad (9)$$

where  $k_{2,ads}$  is the rate constant of second-order equation ( $\text{g/mg min}$ ) [23,52,53]. The values of  $q_e$  and  $k_{2,ad}$  can be calculated from the slope and intercept of the plot of  $t/q_t$  vs.  $t$ , respectively. The results of kinetic study are provided in Table 6. According to the higher correlation coefficient of the pseudo-second-order model ( $R^2 = 0.977$ ) in comparison with the pseudo-first-order model ( $R^2 = 0.949$ ), it can be stated that the adsorption of DB71 onto biosilica/CA nanobiocomposite follows pseudo-second-order kinetic model. This demonstrated that several mechanisms are involved in the adsorption of DB71. Additionally, fitness of the adsorption process to the pseudo-second-order kinetic model indicated that chemical adsorption is the sole rate-limiting step for the adsorption of DB71 onto biosilica/CA nanobiocomposite [6,8,51]. Generally, it has been exhibited that the kinetic adsorption is generally better described by the pseudo-second-order kinetic model for the adsorption of both cationic and anionic dyes in aqueous solutions [51,54].

### 3.7. Isotherm study

To carry out the isotherm study, initial DB71 concentration was varied between 10 and 50  $\text{mg/L}$ , while adsorbent dosage, contact time, and initial pH were constant at 1.5  $\text{g/L}$ , 60 min, and 7, respectively. The linearized forms of Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models were used to describe the adsorption of DB71 onto biosilica/CA nanobiocomposite. The linearized form of Langmuir isotherm model is exhibited in Eq. (10):

$$C_e/q_e = 1/Kq_m + C_e/q_m \quad (10)$$

where  $q_m$  ( $\text{mg/g}$ ) and  $K$  ( $\text{L/mg}$ ) are the maximum amount of adsorbed dye molecules and the affinity of the binding sites for sequestering the adsorbate (Langmuir constant), respectively [14,34]. The values of  $q_m$  and  $K$  can be calculated from the slope and

Table 5

The results of thermodynamic study for the adsorption of DB71 onto biosilica/CA nanobiocomposite

Temperature (K)	$(\Delta G^\circ)$ (kJ/mol)	$(\Delta S^\circ)$ (kJ/mol K)	$(\Delta H^\circ)$ (kJ/mol)
298	−0.474	−0.023	−7.311
303	−0.340		
308	−0.263		
313	−0.118		
318	−0.011		

Table 6

The results of kinetic study for the adsorption of DB71 onto biosilica/CA nanobiocomposite

Type of kinetic model	Value
<i>Pseudo-first-order model</i>	
$R^2$	0.949
$k_{1,ads}$ (1/min)	0.044
$q_e$ (mg/g)	14.29
<i>Pseudo-second-order model</i>	
$R^2$	0.977
$k_{2,ads}$ (g/mg min)	0.004
$q_e$ (mg/g)	18.59
$q_{experimental}$ (mg/g)	16.81

intercept of the plot of  $C_e/q_e$  vs.  $C_e$ , respectively. The linearized form of Freundlich isotherm model is shown through Eq. (11):

$$\log q_e = \log K_F + 1/n \log C_e \quad (11)$$

where  $q_e$  (mg/g) is the amount of adsorbed dye and  $C_e$  (mg/L) is the residual dye concentration in solution. The sorption capacity and sorption intensity can be determined via  $K_F$  (L/g) and  $n$  as Freundlich constants, respectively [5,46]. The values of  $K_F$  and  $n$  were calculated from intercept and slope of the plot of  $\log q_e$  vs.  $\log C_e$ , respectively. The application of D-R isotherm model can be useful to determine whether the adsorption process is chemical or not. The linear form of D-R isotherm model and corresponding parameters were characterized via Eqs. (12) and (13):

$$\ln Q = \ln Q_m - k\varepsilon^2 \quad (12)$$

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (13)$$

where  $Q$ ,  $Q_0$ ,  $k$ ,  $\varepsilon$ ,  $R$ , and  $T$  are the amount of adsorbed dye (mol/g), adsorption capacity (mol/g), adsorption energy ( $\text{mol}^2/\text{J}^2$ ), Polanyi potential ( $\text{J}^2/\text{mol}^2$ ), universal gas constant (8.314 J/mol K), and temperature (K), respectively [23,34]. The values of  $Q_0$  and  $k$  were obtained from intercept and slope of the plot of  $\log Q$  vs.  $\varepsilon^2$ , respectively. The results of isotherm study are provided in Table 7. As result, the Langmuir isotherm model was the best isotherm model for describing the adsorption of DB71 onto the nanobiocomposite ( $R^2 = 0.994$ ) with a maximum adsorption capacity of 21.32 mg/g. In accordance with our results, Salehi and coworkers found that the adsorption of Direct Blue 78 onto chitosan–zinc oxide nanoparticle was well fitted to Langmuir isotherm model [14]. The separation factor ( $R_L$ ) associated with the Langmuir isotherm

Table 7

Isotherm parameters for the adsorption of DB71 onto biosilica/CA nanobiocomposite

Type of isotherm models	Values
<i>Langmuir isotherm</i>	
$q_{\max}$ (mg/g)	21.32
$K$ (L/mg)	0.0193
$R_L$	0.510–0.838
$R^2$	0.9940
<i>Freundlich isotherm</i>	
$K_F$ (L/g)	5.379
$n$	2.611
$R^2$	0.8980
<i>Dubinin–Radushkevich (D–R) isotherm</i>	
$k$ ( $\text{mol}^2/\text{J}^2$ )	$3 \times 10^{-9}$
$Q^0$ (mol/g)	0.0001
$E$ (kJ/mol)	12.91
$R^2$	0.9142

model was used to specify the suitability of the adsorption process as expressed via Eq. (14):

$$R_L = 1/(1 + C_0K) \quad (14)$$

where  $C_0$  is the initial adsorbate concentration (mg/L) and  $K$  is the Langmuir constant (L/mg). If the values of  $R_L$  are between 0 and 1, the adsorption process would be favorable [39,52,55]. Thus, the obtained values for  $R_L$ , which were between 0.510 and 0.838, indicated that the adsorption of DB71 onto biosilica/CA nanobiocomposite would be favorable. In the following, the mean free energy of adsorption ( $E$ ) was calculated and used to determine the nature of the process as shown in Eq. (15):

$$E = 1/(-2k)^{0.5} \quad (15)$$

If the value of  $E$  is between 8 and 16 kJ/mol, the adsorption process is chemical. Alternatively, if the value of  $E$  is less than 8 kJ/mol, the process would be physical [23,34]. The value of  $E$  for the adsorption of DB71 onto biosilica/CA nanobiocomposite was obtained to be 12.91 kJ/mol, confirming chemical nature of the adsorption process.

#### 4. Conclusions

In the present work, nano-sized biosilica was entrapped by CA and used for removing a textile dye in aqueous solutions. CCD statistical approach was



employed to vigorously evaluate the effect of operational parameters on the decolorization and to determine the optimum values of operational parameters for the highest color removal. For a color removal of 81.49%, the initial dye concentration, adsorbent dosage, contact time, and initial pH were identified to be 21 mg/L, 2.4 g/L, 42 min, and 7, respectively. Thermodynamic parameters indicated spontaneous and exothermic nature of the adsorption process. The results of isotherm study showed that the adsorption of DB71 obeyed Langmuir model with the maximum adsorption capacity of 21.32 mg/g. In addition, the mean free energy of adsorption ( $E$ ) revealed the chemical nature of the adsorption process. Conclusively, the application of nano-sized biosilica in immobilized form could be an efficient approach for treating colored effluents.

### Acknowledgments

The authors would like to thank Arak University of Medical Sciences (Iran) and University of Tabriz (Iran) for their financial and instrumental supports.

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