Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1060903

57 (2016) 14051–14059
June

Taylor & Francis
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Optimization and modeling of process variables for adsorption of Basic Blue 41 on NaOH-modified rice husk using response surface methodology

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Received 6 December 2014; Accepted 6 June 2015

ABSTRACT

The aim of this study was to optimize the conditions of the Basic Blue 41 (BB41) adsorption on NaOH-modified rice husk (NaOH–RH) using response surface methodology based on Box–Behnken design. The three-level factors considered were pH (4, 7, and 10), initial concentration of BB41 (50, 75, and 100 mg L^{-1}), and adsorbent dose (0.025, 0.0875, and 0.15 g L^{-1}). Statistical analysis of result has shown that the predicted values for BB41 adsorption were close to the experimental values and were in a good agreement, on the other hand, the *F*-value (40.48), *p*-value (0.0004), and R^2 (0.9865) indicated that the regression is able to give a good prediction of response for the adsorption process in the range studied. According to the results, when the response was set in maximize and all the three factors were set in a range, the optimized values for BB41 adsorption were predicted as follows: pH value of 8.47, and BB41 initial concentration of 67.9 mg L^{-1} and adsorbent dose of 0.12 g L^{-1} for removal efficiency of 97.65%.

Keywords: Adsorption; Agricultural waste; Basic Blue 41; Dye; Optimization; Rice husk

1. Introduction

In recent years, chemical pollution of water resources due to various industrial activities has become a serious environmental problem. In some industries such as textile, leather, paper, plastics, carpet, food, and cosmetics, the presence of synthetic dyes in effluents is a major concern due to their adverse effects [1,2]. Almost all synthetic dyes, the azo dyes (one of the most common group of dyes applied in textile factories), are found to be toxic, carcinogenic, and/or mutagenic, and on the other hand, they are biologically nondegradable; thus, the removal of these dyes from aqueous solution is very important [3].

There are several physical, chemical, and biological methods used in the dye removal from aqueous solution such as adsorption, membrane, coagulation,

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chemical and photochemical degradation, and enzymatic treatment [4–9]. Among these methods, adsorption is proved to be an effective and cost-effective method for many contaminant removals from aqueous solution, especially dye removal [7–18]. In recent years, several adsorbents have been recommended in the literature for the adsorption of dye from aqueous solution that one of the most widely used of them is rice husk which is known as an agricultural waste. Rice husk has attracted increasing attention because of its high adsorption capacity, low cost, and high availability [19].

Rice husk has been studied during the past years by various authors and has been reported to have the potential for the removal of dyes such as direct red-31 and direct orange-26 [20], malachite green [21], methylene blue [22], [21,22] crystal violet [23], and methylene blue [24]. Also, various researchers have used rice husk as a low-cost adsorbent for the removal of pollutants such as oil and oil products [25], humic acids [26], dibenzothiophenes [27], heavy metals [28], and cadmium. [29]. There are several methods to modify the rice husk such as alkali or acidic treatment that has been demonstrated to improve the adsorption properties. NaOH removes impurity compounds from the rice husk surface and revealing chemically reactive functional groups such as –OH.

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for developing and optimizing processes. The general applications of RSM are in the processes research, where several independent variables influence the dependent results of the process [30]. So, it is a powerful method used to determine the influence of variables on adsorption process and it can illustrate the factors that show more impact on adsorption and interaction of them [31,32]. One of the main purpose of RSM is to determine the optimum operational conditions for the process [33]. This implies determining the levels of independent input variables that result in maximum or optimum output, so it can be used for optimization and modeling of the adsorption process. In addition, need to fewer runs is one of the most important advantages of RSM that results in saving chemicals, times, and money. The Box–Behnken design (BBD) is a good design for RSM because it includes estimation of the factors of the quadratic model, building of sequential designs, and detection of lack of fit of the model [32]. In addition, BBD has some advantages to other designs of RSM and a comparison has demonstrated that the BBD is more efficient than other designs [32]. So the aim of this study was to investigate the adsorption efficiency of BB41 as a model of basic dye from aqueous solutions using NaOH-treated rice husk by applying RSM. In addition to determine the best condition of BB41 adsorption and to optimization of process, BBD was applied.

2. Materials and methods

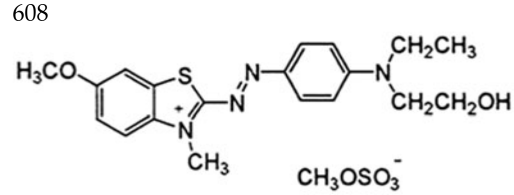
2.1. Chemicals

Sodium hydroxide (NaOH) and synthetic dye BB41 (see Table 1) were purchased from Merck (Darmstadt, Germany) and Alvan Sabet Co. (Tehran, Iran), respectively. All other reagents and chemicals were of the highest purity available.

2.2. Preparation of adsorbent

The adsorbent rice husk used in the present experiments was prepared by alkali treatment using the

Table 1
General characteristics of the dye BB41

Parameter	Characteristic
Chemical name	Basic Blue 41
C.I. number	11105
Classification	Single azo
Apparent color	Blue
Molecular weight	482.57
Molecular formula	$C_{20}H_{26}N_4O_6S_2$
λ_{max} (nm)	608
Chemical structure	

method described in our previous work [5]. Briefly, the natural rice husk (NRH) was screened and passed through 2 mm sieve size, followed by washing repeatedly by distilled water. After that it was dried in 25°C for 2 d. Alkali treatment was carried out by immersing the rice husk samples in contact with 5% solution of NaOH and placed in autoclave at 121°C for 15 min at 10 psi. Then, it was filtered and washed many times with distilled water. After drying modified rice husk at 25°C for 2 d, it was then applied to adsorption experiments. In order to determine the surface structure and morphology of natural and modified rice husk, X-ray diffraction (XRD) and SEM analyses were carried.

2.3. Dye solution and analytical method

The BB41 stock solution containing 1,000 mg L^{-1} was prepared by dissolving BB41 powders in distilled water. BB41 working solutions in different concentrations were prepared by diluting the BB41 stock solution with distilled water. The pH values of the BB41 working solution were adjusted with diluted HCl and NaOH and were measured by pH meter (metrohm, 827 pH laboratory) before adsorption experiments. The analysis of BB41 was done using UV–vis spectrophotometer (Shimadzu UV 1700, Japan) at the maximum absorbance wavelength 608 nm.

2.4. Batch adsorption experiments

In order to study the adsorption of BB41 on NaOH–RH, the experiments were performed using batch reactor. For each run, weighted amounts of NaOH–RH were added to a 250-mL Erlenmeyer flasks containing 100 mL of BB41 solution and pH was adjusted to the desired value using 0.1 M NaOH or 0.1 M HCl solutions according to the pH, concentrations of BB41, and adsorbent dose in Tables 2 and 3.

The Erlenmeyer flasks were agitated in a rotary shaker at 150 rpm for 1 h (as equilibrium time, which testified in the first of experiments). After adsorption, samples were centrifuged at 4,000 rpm for 10 min and the concentration of BB41 in supernatant was analyzed.

The BB41 adsorption efficiency (%R) was defined as the percentage of initial BB41 that was removed from the solution during the adsorption process and was calculated as follows (Eq. (1)):

$$\%R = \frac{C_{(\mathrm{BB41})0} - C_{(\mathrm{BB41})t}}{C_{(BB41)0}} \times 100 \tag{1}$$

where $C_{(\mathrm{BB41})0}$ and $C_{(\mathrm{BB41})t}$ are the initial and final concentration (mg L^{-1}) of BB41. All the experiments were performed in triplicate and the average of responses (presented in the Table 3) was used to further analyze statically.

2.5. Statistical design of experiments

In order to determine the factors that influence the removal of BB41 by NaOH–RH and to investigate the interaction effects between various factors and determine the best conditions for BB41 adsorption, a three-level, three-factor, RSM and BBD of experiments were applied. For this purpose, three factors, namely pH, initial concentration of BB41, and adsorbent dose, were varied at three levels (−1, 0, +1), as shown in Table 2. A total of 15 experiments were performed. This value was obtained from Eq. (2):

$$N = 2X(X-1) + Y = 2 \times 3(3-1) + 3 = 15 \tag{2}$$

where N is the total number of experiments, X is the number of variables, and Y is number of replicates at the center point.

After analyzing the data obtained from experiments by applying the analysis of variance (ANOVA) using Design-Expert version 7.0.0 (Stat-Ease, trial version) software, the experimental data were fitted to a quadratic polynomial model, expressed by Eq. (3):

$$R = X_0 + X_1A + X_2B + X_3C + X_4AB + X_5AC + X_6BC + X_7AA + X_8BB + X_9CC \tag{3}$$

Table 2
Three factors BBD of variables (ranges and levels)

Independent variables	Coded symbol	Code levels		
		−1	0	1
pH	A	4	7	10
Initial concentration of dye (mg L^{-1})	B	50	75	100
Adsorbent dose (g L^{-1})	C	0.025	0.0875	0.15

Table 3
BBD matrix of variables along with actual, fits, and residual values

Run number	*A*	*B*	*C*	(%) Color removal	Fit for color removal	Residuals for color removal
1	0	1	1	87	88.19	−1.19
2	0	1	−1	57	57.31	−0.31
3	1	1	0	85	85.94	−0.94
4	0	0	0	90	91	−1.00
5	1	−1	0	95	97.44	−2.44
6	−1	1	0	75	72.56	2.44
7	1	0	−1	80	78.75	1.25
8	0	−1	−1	76	74.81	1.19
9	0	−1	1	93	92.69	0.31
10	1	0	1	97.5	95.38	2.13
11	0	0	0	91	91	0
12	−1	0	−1	55	57.13	−2.13
13	−1	−1	0	84	83.06	0.94
14	−1	0	1	88	89.25	−1.25
15	0	0	0	92	91	1

where R is the predicted adsorption percentage of BB41, X_0 is the intercept of model, X_{1-9} are the estimated coefficients, and A, B, and C are the coded factors (Table 2).

3. Results and discussion

3.1. Characteristic of natural and modified RH

XRD analysis was carried out to identify the characteristic of NRH and NaOH–RH. According to Fig. 1, the XRD analysis shows that there is an increase in the intensity of NaOH–RH compared to that NRH. It may be illustrated by this fact that alkali treatment eliminates the impurities such as waxes and fats from the surface of NRH.

Fig. 2(a) and (b) shows the micrograph of NRH and NaOH–RH. According to Fig. 2(b), the morphology of NaOH–RH showed that the surface was highly roughness compared to the NRH (Fig. 2(a)), due to the surface of rice husk was changed by NaOH treatment and the pores on the surface converted to very heterogeneous pores.

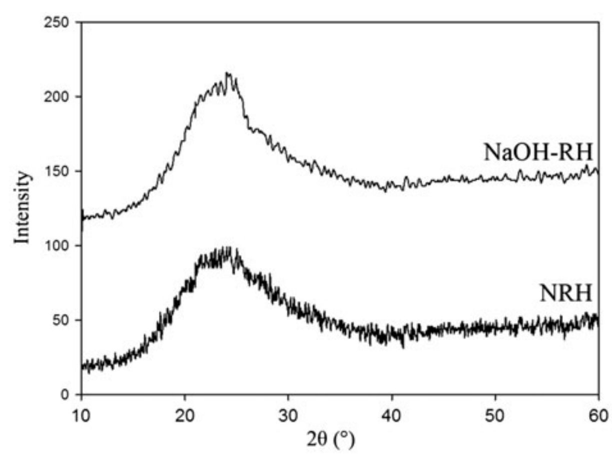


Fig. 1. XRD diffraction of NRH and NaOH–RH.

3.2. Design of experiments

By Design-Expert version 7.0.0 (Stat-Ease, trial version) software, RSM based on BBD was applied for the experimental design throughout the adsorption process study. A total of twelve sets of experiments and three replicates at the center point (0, 0, 0) were used to demonstrate the statistical significance of the independent factors; pH (A), initial concentration of dye (B), and adsorbent dose (C) in three levels (−1, 0, +1), on BB41 adsorption as the dependent variables (responses) by NaOH–RH. The range and levels of the factors investigated in this study are shown in Table 2 while Table 3 shows the experimental design, actual, predicted, and residual values of the BB41 removal efficiency.

3.3. Analysis of variance (ANOVA)

ANOVA was used to analyze experimental data, and the adequacy of a quadratic model was examined by F-value, p-value, and R^2. According to the ANOVA in Table 4, the computed F-value (40.48) and p-value (0.0004) implied that the model was significant with low probability (lower than 0.05). By substituting the

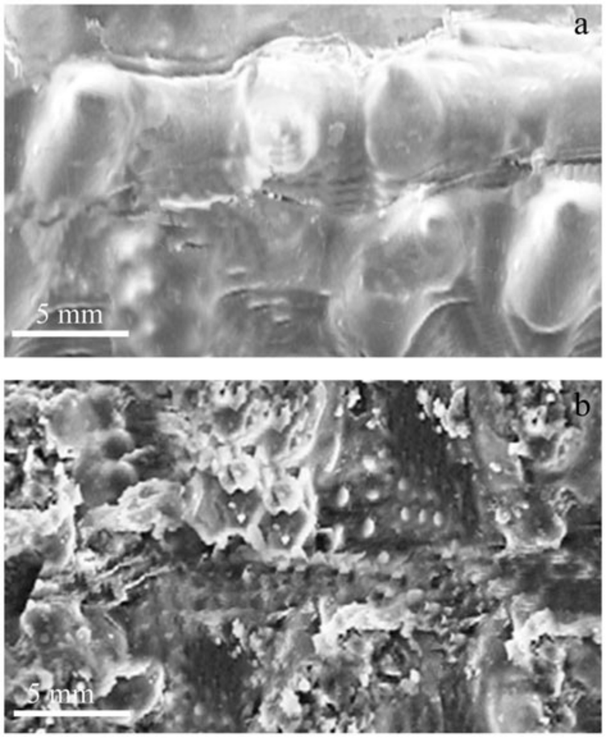


Fig. 2. SEM for NRH (a) and NaOH–RH (b).

coefficients Xi of significant effects in Eq. (3) by their values, the quadratic equation for BB41 removal using pH (A), initial concentration of dye (B), and adsorbent dose (C) as the main variables was as follows:

$$R = 91 + 6.94A - 5.5B + 12.19C - 3.87AC + 3.25BC - 4.06BB - 8.69CC \quad (4)$$

where R is the % removal of BB41; A, B, and C are the coded values of the factors in Table 2.

Results obtained sufficiently suggest that the quadratic model was in good prediction of the experiments, and the terms in the model have a significant effect on the response. In addition, according to the p-value (0.0958) of the lack of fit that was found insignificant, the model was desirably fit.

The main effect of adsorbent dose (F-value = 192.82) was found to be the most significant factor to have the largest effect toward the BB41 adsorption efficiency and this was followed by the main effect of pH (F-value = 62.48) and the main effect of initial concentration of BB41 (F-value = 39.27). On the other hand, this founding was consistent with Eq. (4), in which the

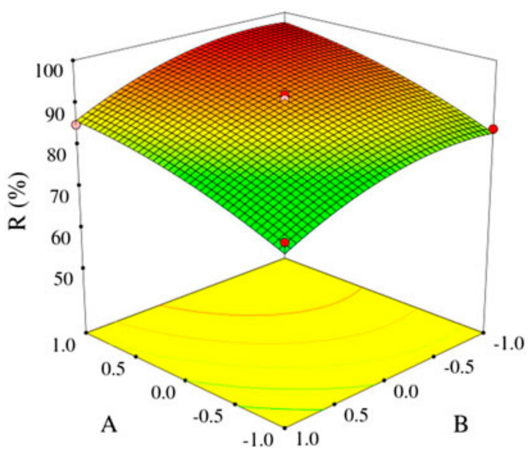


Fig. 3. 3D Plot of interaction effect for BB41 adsorption (%R) between pH (A) and BB41 initial concentration (B).

Table 4
Analysis of variance (ANOVA) of BB41 removal model

Source	Sum of squares	DF	Mean square	F-value	p-value Prob. > F	Status
Model	2,245.42	9	249.49	40.48	0.0004	Significant
A	385.03	1	385.03	62.48	0.0005	
B	242	1	242	39.27	0.0015	
C	1,188.28	1	1,188.28	192.82	<0.0001	
AB	0.25	1	0.25	0.04	0.8483	
AC	60.06	1	60.06	9.74	0.0262	
BC	42.25	1	42.25	6.85	0.0472	
A^2	17.67	1	17.67	2.87	0.1512	
B^2	60.94	1	60.93	9.89	0.0255	
C^2	278.67	1	278.66	45.22	0.0011	
Residual error	30.81	5	6.16			
Lack of fit	28.81	3	9.60	9.60	0.0958	Not significant
Pure error	2	2	1			
Core total	2,276.23	14				

main effect of adsorbent dose has the largest coefficient (+12.19) followed by the main effect of pH (+6.9), and the main effect of initial concentration of BB41 (−5.5).

Enhanced adsorption of BB41 as a cationic dye on NaOH–RH with increase in pH of solution can be explained on the basis of the competitive adsorption of H^+ and OH^- ions with the NaOH–RH. NaOH–RH absorb H^+ ions at lower pH due to the presence of H^+ ions in the solution, while it is active for the adsorption of cationic substance at higher pH due to the deposition of OH^- ions. The adsorbent dose has been recognized as the most important factor influencing adsorption process. According to Eq. (4), adsorbent dose has positive effect on the adsorption of BB41 by NaOH–RH, and the removal of BB41 increases with increase in adsorbent dose due to the availability of greater surface area and more adsorption sites. It can be realized from the Eq. (4) that the rate of BB41 adsorption is a function of the initial concentration of the NaOH–RH and the amount of BB41 adsorbed per unit of NaOH–RH increases with increasing initial concentration of dye; however, the adsorption percentage decreased.

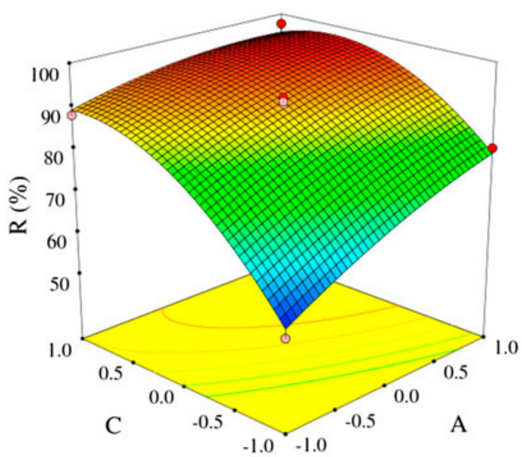


Fig. 4. 3D Plot of interaction effect for BB41 adsorption (%R) between pH (A) and adsorbent dose (C).

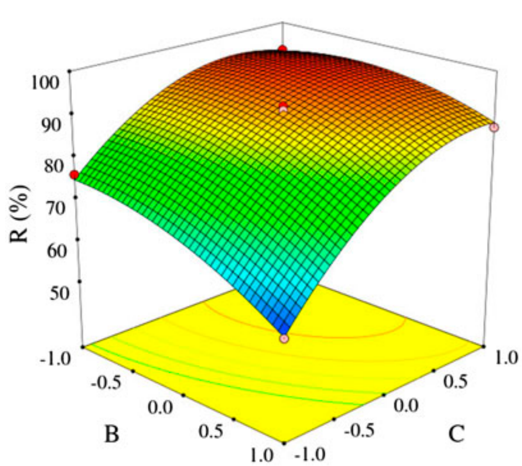


Fig. 5. 3D Plot of interaction effect for BB41 adsorption (%R) between BB41 initial concentration (B) and adsorbent dose (C).

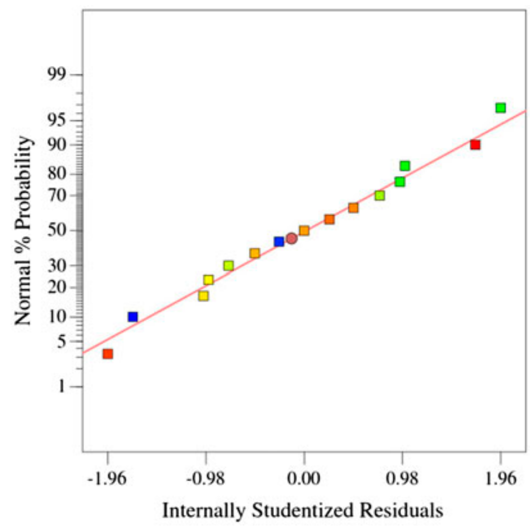


Fig. 6. Normal probability plot of residual for BB41 adsorption.

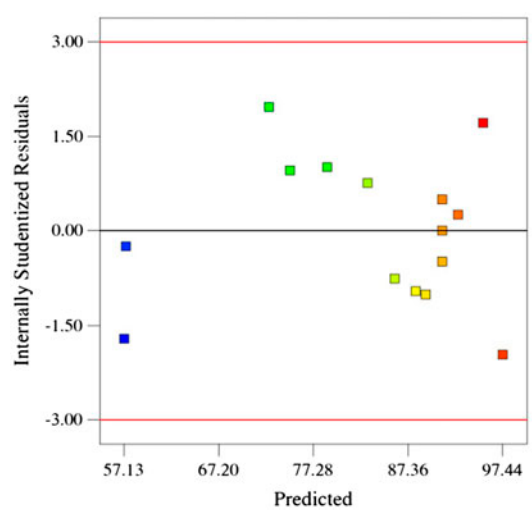


Fig. 7. Plot of residual against predicted response.

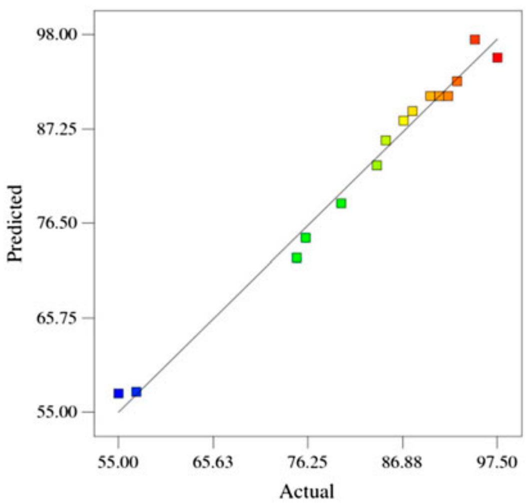


Fig. 8. Comparison between the actual values and the predicted values of RSM model.

The 3D plots for the interaction effects of, *AB*, *AC*, and *BC* on the removal of BB41 by NaOH–RH were shown in Figs. 3–5.

As shown in Fig. 3, according to the *p*-value of *AB* obtained by ANOVA (Table 4), the interaction effect between pH and initial concentration of BB41 is statically not significant (*p*-value = 0.8483) . However, the interaction effect between pH and adsorbent dose in Fig. 4 with the *p*-value of 0.3841 and the interaction effect between initial concentration of BB41 and adsorbent dose with the *p*-value of 0.8596 (Fig. 5) are statically significant.

It is observed from Fig. 4 that as there was an increase in pH, the removal efficiency increased with an increase in adsorbent dose up to the optimum level. Although it can be realized from Fig. 5, as there was an increase in adsorbent dose, removal efficiency increased with a decrease in BB41 initial concentration up to the optimum level.

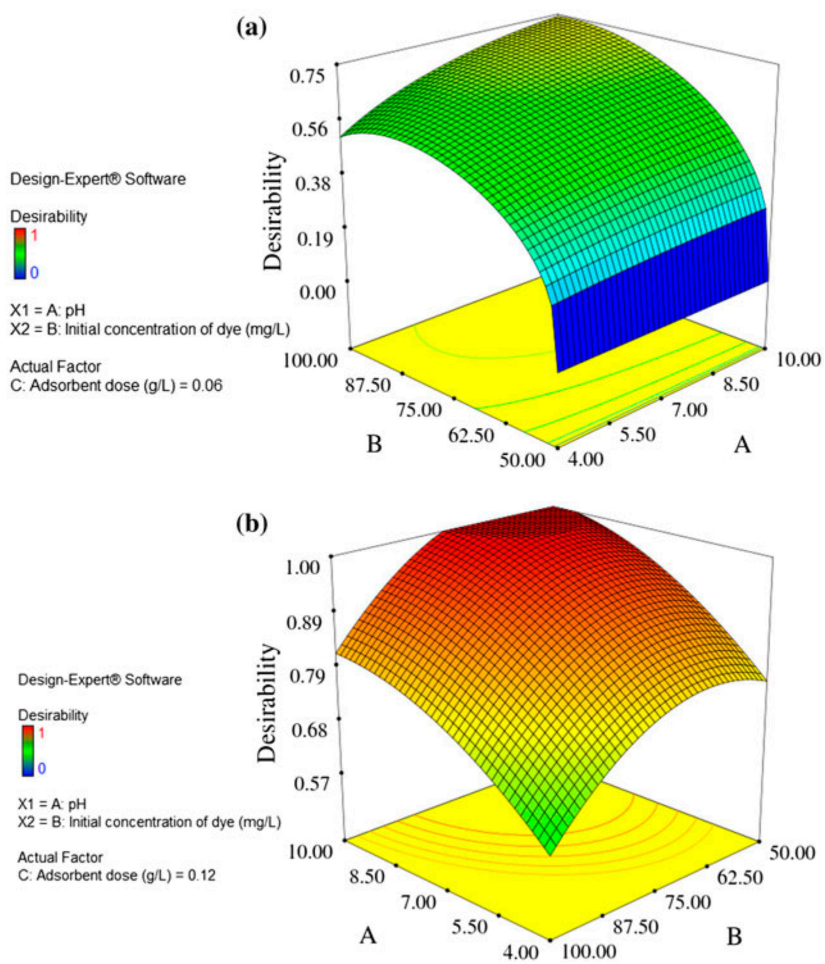


Fig. 9. 3D plots of desirability for BB41 adsorption on NaOH–RH.

3.4. Adequacy of model

Analyses on normal probability plot of the residuals with a 95% confidence (Fig. 6) depicted a straight line residuals distribution, which denoting errors are evenly distributed and therefore support adequacy of the least square fit and it is evident that the data from the experiments come from a normally distributed population. Although results illustrated in Fig. 7 revealed that the model proposed is adequate and reasonably free from any violation of the independence, as internally studentized residuals are equally tabulated within the acceptable limit (values between −3 and +3) and confirm that they are in the reliable range.

In addition, parity plot of the BB41 removal data with the model predictions at 95% confidence interval vs. the experimental adsorption is shown in Fig. 8. The correlation coefficient for the plot is 0.9865, which indicates that the model is able to give a reasonably good estimate of response and also indicates the good performance for the model.

3.5. Optimization

To maximize the BB41 adsorption efficiency, the optimum adsorption conditions were calculated using the Design-Expert version 7.0.0 (Stat-Ease, trial version) software. In criteria step of optimization, two different optimizations were carried out by setting different criteria. When the response was set in maximize, pH in range, BB41 initial concentration in maximize, and adsorbent dose in minimize, the optimum conditions for BB41 adsorption were predicted as follows (Fig. 9(a)): pH value of 10, and BB41 initial concentration of 96.55 mg L^{-1} and adsorbent dose of 0.06 g L^{-1} for removal efficiency of 81.45%. Although the response was set in maximize and the factors (*A*, *B*, and *C*) were set in a range, the optimum conditions for BB41 adsorption were predicted as follows (Fig. 9(b)): pH value of 8.47, and BB41 initial concentration of 67.9 mg L^{-1} and adsorbent dose of 0.12 g L^{-1} for removal efficiency of 97.65%.

4. Conclusion

Rice husk was modified by alkali treatment using NaOH and used for the adsorption of BB41 dye from aqueous solution. RSM based on BBD applied in order to optimize of the conditions of adsorption. A quadratic model was developed to correlate the three factors to the BB41 adsorption. Through analysis of the response surfaces derived from the model, the main effects of all the three factors (pH, initial concentration of BB41, and adsorbent dose) were found to have significant effects on the BB41 adsorption on NaOH–RH. While the interaction effects of *AC* and *BC* were found to have significant effect and the interaction effect of the *AB* was found to have insignificant. According to the ANOVA, the computed *F*-value (40.48) and *p*-value (0.0004) with the R^2 of 0.9865 implied that the model was significant and the quadratic model was in good prediction of the experiments and the terms in the model have a significant effect on the response.

The adsorption capacity was 650 and 35.43 mg/g, for the NaOH–RH and NRH, respectively. So, it can be realized that NaOH–RH has good adsorptive characteristics for the adsorption of BB41 dye from aqueous solution. However, the NRH was not a good adsorbent for BB41. Thus, this modifying method can be useful for the modification of rice husk for enhancing the capacity of adsorption and this shows the modification is effective.

Acknowledgment

This work was supported by the Institute for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran.

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